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# CHEMICAL DURABILITY OF PORCELAIN ENAMELS*

By Ralph L. Cook and Andrew I. Andrews

Abstract

The resistance of representative porcelain enamel surfaces to the chemical attack of different concentrations of various solutions was investigated in considerable detail. Cylindrical cup-shaped samples were coated with (1) a ground coat, (2) a white fluoride cover enamel, (3) a white antimony cover enamel, (4) a white zirconium cover enamel, (5) an acid-resistant white cover enamel, (6) a sign blue cover enamel, (7) a blue zirconium enamel, and (8) a chemical acidproof blue cover enamel. The loss in weight of these enamel surfaces, after exposure to chemical attack, was determined at definite time intervals. The solutions studied consisted of different concentrations of the inorganic acids, alkalis, several organic acids, as well as selected salt solutions at both room and boiling temperatures.

Numerous curves are presented showing the comparative chemical durability of the various porcelain enamel surfaces in which the cumulative loss in weight is plotted against time. Several photomicrographs show the nature and type of chemical attack on the different surfaces.

The porcelain enamel surfaces showed considerable variation in their resistance to the chemical attack of the various solutions. All of the porcelain enamels were, in general, resistant to attack at room temperature by the alkali and salt solutions. The acid-resistant and acidproof enamels were resistant to the action of both inorganic and organic acids at room and at boiling temperatures; a wide variance, however, was shown in the comparative acid resistance of the non-acid-resisting enamel to the attack of either organic acids or inorganic acids at room temperature. All porcelain enamels showed equally low resistance to boiling alkali solutions, but some of the enamel surfaces were attacked markedly by the boiling salt solutions.

## I. Introduction

The chemical durability or solubility of porcelain enamels has long been a subject of considerable investigation, as this particular property directly influences their usefulness. In the household, porcelain enamels are subjected to acid fruit juices, alkaline washing powders, soaps, and water containing a variable amount of dissolved salts. In hospital use, porcelain enamel surfaces must be resistant to the attack of organic and inorganic acids and salt solutions at normal and boiling temperatures. In industrial applications, a wide variety of equipment, such as tanks, kettles, digesters, and autoclaves used in the chemical process industry, is enameled, and these surfaces are required to resist high chemically active solutions at room and elevated temperatures. In recent years, the field of industrial applications of porcelain enamels has had a marked increase owing to the restrictions placed on the highly strategic war metals, nickel, aluminum, Monel, and stainless steel.

The solubilities of different porcelain enamels vary over a broad range, some being insoluble over prolonged periods while others are attacked to a pronounced degree in a relatively short time. The porcelain enamel surface, which has been attacked by an acid or alkali, loses its gloss, becoming iridescent or rough and, in many cases, exhibits a highly etched condition. The enamels, which are very soluble, lose their pronounced glassy structure and appear as a powdery dust that can be scraped from the metal.

The purpose of the present investigation was to determine the chemical durability of commercially representative porcelain enamels to the attack of various inorganic and organic acids, alkalis, and selected salt solutions at room and at boiling temperatures. The porcelain enamel surfaces which were selected for this study included a ground coat, a fluoride white cover, an antimony white cover, a zirconium white cover, an acid-resistant white cover, a sign blue cover, a blue zirconium cover, and a chemical acidproof cover en-

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amel. In determining the attack of the different chemical solutions on the various porcelain enamel surfaces, it was felt that a quantitative expression of the actual loss in weight per unit area at selected time intervals would most clearly indicate the rate of attack and the degree of total attack.

## II. Review of Previous Investigations

In reviewing the literature on the chemical durability of porcelain enamel surfaces, the number of different kinds of tests and the variety of the conditions under which these tests were run are particularly impressive. These tests, in general, may be classified into three main groups, (1) the grain test, (2) the spot test, and (3) the loss-in-weight test.

### (1) Grain Test

This test consists of subjecting a weighed amount of the powdered enamel frit to acid for a definite length of time; the enamel powder is filtered and reweighed and the loss in weight represents the amount of acid attack.

Poste,[1] using the grain test, subjected finely powdered grains of frit to the action of various concentrations of acetic, hydrochloric, sulfuric, and nitric acids at room temperature for 24 hours and found that the loss in weight of the frit grains increased as the strength of the acid was increased to approximately 10% and then decreased rapidly. Staley,[2] in a discussion of Poste's results, presented data showing the electrical conductivity at different acid strengths for sulfuric, nitric, hydrochloric, and acetic acids. The hydrochloric acid showed the maximum ionic activity at 20%, the acetic at 15%, and the sulfuric and nitric acids at about 30%. Poste,[3] in later work in conjunction with The American Ceramic Society Committee on Standards, investigated the effect of different concentrations of citric and tartaric acids on five commercial frits and concluded that these acids are more active and subject to less variation than acetic acid. He also reported that there was no marked effect from different-sized frit grains. In further work, Poste[4] concluded that a 15.73% solution of citric acid was desirable as the standard acid solution; and in another article,[5] he showed that ground-coat frit was less resistant to the action of citric acid than the white cover-coat frits.

Uchida and Arimoto[6] studied the resistance of frit grains to the action of a 10% solution of sulfuric acid for 48 hours at 20°C. and attempted to correlate the acid action with variations in the frit composition.

Andrews[7] made use of a grain test in which 20- to 30-mesh frit was subjected to the attack of a 20% solution of hydrochloric acid at 100°C. for three hours and then immediately filtered through a weighed Gooch filter. He concluded that the test was only fairly reliable but that it was particularly useful where the frits tested were not essentially different in composition.

The use of the grain test under carefully controlled conditions gives satisfactory results, but since no standard conditions have been agreed to, the tests made by different investigators are not readily compared. The kind of acid and its strength, the temperature, the grain size of the frit, and the time of exposure are important factors which would have to be considered in carrying out this test. It is subject to the further criticism that the degree of acid attack is proportional to the surface area and not to the weight of frit. In view of the fact that there is no convenient way of determining the surface area of the frit particles, the test is subject to considerable criticism even under the most favorable conditions.

### (2) Spot Test

The spot test is an actual simulated service test and consists of placing several drops of acid on a fired porcelain enamel surface and noting the degree of attack after a definite time interval. One of the first spot tests, reported by the Committee on Standards of The American Ceramic Society,[5] consisted of placing a drop of acid on a horizontal enamel surface, allowing it to remain one minute, and wiping the spot with a damp sponge. A reduction in specular reflection indicated acid attack. It was reported that a 1% solution of citric acid affected most of the enameled cooking utensils on the market and even a 1% acetic acid solution caused a slight diminution in specular reflection in the better-grade ware. It was suggested that the test could be made quantitative by determining the strength of acid that would just affect the enamel surface. Shaw,[8] in an investigation on white enamels for sheet steel, tested the enamels with lemon juice and 10% solutions of citric and oxalic acids. The solutions were dropped on the enamel surface and allowed to remain for periods of 10 and 30 minutes or until they evaporated to dryness. The degree of attack was judged by the appearance of the enamel.

Other investigators, Danielson and Sweely,[9] Wolfram,[10] and Wolfram and Harrison,[11] used a 1% solution of acetic acid for various time periods in determining the acid resistance of enamels.

In a similar type of spot test, Andrews[7] placed a few drops of a 7% citric acid solution on the finished enamel for 15 minutes. The degree of attack was used to

[1] E. P. Poste, "Relative Action of Acids on Enamels," *Trans. Amer. Ceram. Soc.*, **17**, 137–44 (1915).

[2] H. F. Staley, discussion of Poste paper, *ibid.*, pp. 144–48.

[3] E. P. Poste, "Relative Action of Acids on Enamels, III," *Jour. Amer. Ceram. Soc.*, **2** [1] 32–43 (1919).

[4] E. P. Poste, "Relative Action of Acids on Enamels, IV," *ibid.*, **3** [7] 560–67 (1920).

[5] E. P. Poste, "Relative Action of Acids on Enamels, V," *ibid.*, **6** [6] 689–97 (1923).

[6] Tokiji Uchida and Kazuo Arimoto, "Study of Acid-Resisting Enamels," *Osaka Indus. Lab. Bull.*, **4**, 68 (1923).

[7] A. I. Andrews, "Acid-Resisting Cover Enamels for Sheet Iron," *Univ. of Ill. Eng. Expt. Station Bull.*, No. 201 (January, 1930); Enamel Bibliography, 1944 ed., p. 11.

[8] J. B. Shaw, "Enamels for Iron and Steel," *Bur. Standards Tech. Paper*, No. 165, 88 pp. (July 22, 1930); pp. 81–85.

[9] R. R. Danielson and B. T. Sweely, "Relation Between Composition and Properties of Enamels for Sheet Steel," *Jour. Amer. Ceram. Soc.*, **6** [10] 1011–19 (1923).

[10] H. G. Wolfram, "Effect of Zirconia in Enamels for Sheet Steel," *ibid.*, **7** [1] 1–13 (1924).

[11] H. G. Wolfram and W. N. Harrison, "Effects of Composition on Properties of Sheet-Steel Enamels," *ibid.*, **8** [11] 735–55 (1925).

determine whether the enamel was soluble, slightly soluble, or acid resisting. Gautsch[12] also made use of a 7% citric acid solution, but the acid was applied to the finished ware by means of 1-in. disks of blotting paper which had been saturated in the acid. The disks were placed on the ware and removed after various time periods from one minute to 24 hours, and the degree of attack on the enamel was expressed as stainless, stained, or etched for the period of time exposed to the test.

Malinovszky[13] subjected cast-iron test plates and sinks to the action of 5, 10, 15, 20, 25% and concentrated hydrochloric acid for 5 minutes and found that the enamels were attacked badly.

Fetterolf,[14] in studying the acid resistance of cast-iron enamel compositions, used a spot test made with 7% citric acid and 7% hydrochloric acid; the action of the 7% hydrochloric acid was found to be the more severe. In another test, a portion of an enameled plate was immersed in 20% hydrochloric acid for 24 hours. In these tests, the enamel surface was examined for staining and loss in gloss.

In April, 1937, the Porcelain Enamel Institute[15] issued a test for acid resistance as a tentative standard, which was adopted as a standard test in July, 1938. The approved test is divided into the commercial, the umpire, and the research tests. In the commercial test, several drops of a 10% solution of citric acid are placed on the enamel specimen to form a pool and immediately covered with a 1-in. inverted watch glass. After 15 minutes of treatment, the watch glass is removed, the solution rinsed from the surface, and the specimen dried with a clean cloth by blotting. After visual examination, the enamel is graded into one of five classes. In the umpire and research tests, one end of a flat enamel panel is coated with shellac and immersed in a 10% solution of citric acid for 15 minutes. In the research test, the same system of classification is used as for the commercial test, but the loss of specular gloss is also determined.

Bryant[16] recommended the determination of the loss in gloss as a measure of the degree of acid attack. In this test, a bell jar fitted with a reflux condenser is clamped on a flat enameled plate. A boiling 2.5% solution of malic acid is kept in contact with the enamel surface for 30 minutes. No correlation was found between loss in gloss and loss in weight in this test.

Spencer-Strong[17] made use of an acid test, which followed closely that of the Porcelain Enamel Institute, in studying various factors, such as the effect of firing time and temperature, drying, and weight of application on acid resistance. Petersen and Hutchison,[18] in studying the effect of different electrolytes in acid-resisting enamels, used a similar spot test.

A desirable feature of the spot test is that the actual surface of the finished enamel is being tested and not the frit as in the grain test. The first sign of attack with the spot test results in an iridescence or slight discoloration of the enamel; in a stronger attack, a surface shows selective marking with a pencil; and finally, with severe attack, the gloss is destroyed and the surface deeply etched.

### (3) Loss-in-Weight Test

The loss in weight of the fired enamel test pieces when exposed to acid has probably been used more extensively than any other test. This test consists of exposing the weighed enamel test piece to the acid of desired strength for a selected time interval; the piece is then washed, dried, and reweighed.

One of the first tests of this nature was proposed in an article by Shaw[19] in which the acid solubility of several enamel compositions was determined and a standard solubility test for sheet-steel cooking utensils was proposed. This test, using one- to two-quart containers, consisted of boiling vigorously a 1% solution of sulfuric acid for 15 minutes and determining the loss in weight. Shaw concluded that ware which showed a solubility greater than 0.008 gm. per sq. in. should be rejected.

Landrum[20] gave a report on a series of tests, using various initial strengths of acetic acid which he boiled to dryness in a weighed enameled test dish. From these data, the degree of attack on enamel surfaces was shown to increase rapidly from 1 to 20% and then to decrease to zero at 100% acetic acid. Frost,[21] using a test procedure similar to that of Poste on a rather soluble alkali borosilicate glaze, found comparable results.

Collins,[22] in testing commercially prepared 6-in. samples of enamel kitchenware, boiled 500 cc. of a 4% solution of acetic acid in the vessels for one-half hour. He stated that a 1% solution of citric or tartaric acid gave results which corresponded with those obtained from the use of 4% acetic acid.

Staley,[23] in studying the acid-resisting properties of various compositions used for chemical ware, selected a constant boiling solution of 20% hydrochloric acid for 1000 hours unless the enamel failed before that time. The point of failure was determined when the enamel

[12] M. C. Gautsch, "Qualitative Spot Test for Resistance of Enamelware to Acids," *Bull. Amer. Ceram. Soc.*, **11** [5] 138 (1932).

[13] A. Malinovszky, "Acid-Resistant Enamels," *Jour. Amer. Ceram. Soc.*, **11** [2] 110–13 (1928).

[14] L. D. Fetterolf, "Acid-Resisting Dry-Process Cast-Iron Enamels and Effect of BaO, PbO, and ZnO," *ibid.*, **15** [1] 1–7 (1932).

[15] "Test for Acid Resistance of Porcelain Enamels," Porcelain Enamel Inst., Technical Research Section, Chicago, 1937; Enamel Bibliography, 1944 ed., p. 271.

[16] E. E. Bryant, "Controlled Boiling Acid Test for Porcelain Enamels," *Jour. Amer. Ceram. Soc.*, **20** [10] 317–19 (1937).

[17] G. H. Spencer-Strong, "Factors Influencing Acid-Resisting Enamels," *ibid.*, **21** [1] 1–8 (1938).

[18] F. A. Petersen and Clark Hutchison, "Electrolytes in Acid-Resisting Enamels," *ibid.*, **24** [2] 51–57 (1941).

[19] J. B. Shaw, "Testing Sheet-Steel Enamels," *Trans. Amer. Ceram. Soc.*, **12**, 463–93 (1910).

[20] R. D. Landrum, "Resistance of Sheet-Steel Enamels to Solution by Acetic Acids of Various Strengths," *ibid.*, **13**, 494–501 (1911).

[21] L. J. Frost, "Action of Acetic Acid Solutions of Different Strengths on Sheet-Steel Enamel," *Jour. Amer. Ceram. Soc.*, **1** [6] 422–28 (1918).

[22] W. D. Collins, "Acid Test on Enamelware," *Ind. Eng. Chem.*, **14**, 8 (1919).

[23] H. F. Staley, "Relation of Compositions to Solubility of Enamels in Acids," *Jour. Amer. Ceram. Soc.*, **4** [9] 703–17 (1921).

surface could be definitely scratched with a pointed knife blade.

Hecht and Oldenburg[24] used weighed enameled steel rods with a hemispheric end and recommended the use of a 5% lactic acid solution.

Dawihl[25] recommended the use of an enameled disk or tube, which was boiled in a 10% formic acid solution for one-half hour and the loss in weight was expressed in milligrams per 100 sq. cm.

Hecht and Hornke[26] reported using a hollow cylindrical test piece, which was subjected to the action of 15% lactic acid or 10% formic acid and the loss in weight determined.

In the Good Housekeeping Institute test,[27] a 2% solution of citric acid or a 4% solution of acetic acid is boiled in the enameled ware for 8 hours, keeping the level constant by additions of acid of the same concentration. After the boiling period, the pan is emptied, rinsed, dried, and examined for etching. The Good Housekeeping Institute does not recognize any degrees of acid resistance, the enamel being considered either acid resistant or, if affected by the test, non-acid resistant.

A recent New South Wales Pure Food Act[28] requires enamel vessels (for the storage or preparation of food) to be free from Sb, Pb, and As; another requirement is that the vessels, when filled with a boiling 0.5% solution of citric acid and allowed to stand for 24 hours, shall not yield, on ignition of the residue obtained when a definite proportion of the solution is evaporated, an amount of ash exceeding 1 mg. per sq. cm. of surface.

Azarov and Savchenko,[29] in work on enamel grains, reported that with 1.5% and 5% solutions of sulfuric acid, the attack increased rapidly at increased pressures up to 5 atmospheres.

A proposed British Standard Test[30] for acid resistance consists of using an enameled container such that 50 sq. cm. are covered with a 3% solution of oxalic acid and then heating on a water bath for one hour. The amount of attack of the hot oxalic acid solution on the enamel is expressed as the amount dissolved in milligrams per square decimeter.

Schmidt,[31] in studying the stability of acidproof enamels to the action of corrosive chemical agents, pointed out that the measurement of the loss in weight for a certain period of time is not sufficient for the accurate determination of the acid solubility of the enamel but that the effect of time on the loss in weight must be considered. He proposed that the quantity of enamel dissolved out by an acid increases logarithmically with time, which is expressed by formula (1).

$$x = 2.3a \log (1 + ct) \qquad (1)$$

$x$ = quantity of enamel dissolved out in time, $t$, from unit surface.
$a$ and $c$ = constants, characteristic of enamel acid resistivity.

Constant $a$ is called the acid-resistance figure, and an enamel is said to be highly resistant if $a$ is less than 0.4 mg. per sq. cm. (2.5 mg. per sq. in.) after treatment with 20% boiling hydrochloric acid.

The Enameled Utensil Manufacturers' Council[32] recently established specifications for a standard solubility test, in which a circular plate, $3^1/_4$ in. in diameter, is cut from the pan to be tested, clamped on the bottom of a glass cylinder which is fitted with a short tube, and subjected to the action of a boiling 6% solution of citric acid for 2.5 hours. The loss in weight resulting from the chemical action is expressed as grams per square inch. At the present time, the standards call for a multiple-coat enamelware to have a loss in weight of not over 0.0125 gm. per sq. in.; and for one-coat ware, a loss in weight of not more than 0.018 gm. per sq. in.

From the foregoing discussion of the loss-in-weight test, it is apparent that various investigators have used acids of different strengths at varied temperatures for various time intervals on widely different enamels.

## III. Experimental Procedure and Details

### (1) Porcelain Enamel Compositions

In the selection of the specific porcelain enamel compositions for the study of the comparative chemical durability of enamel coatings, it seemed desirable to choose those compositions which are typical and representative of commercial practice. The porcelain enamel surfaces selected include the following enamel types: ground coat, sign blue cover, blue zirconium cover, chemical acidproof, fluoride white cover, antimony white cover, zirconium white cover, and a typical acid-resistant white cover.

Table I shows the frit compositions,[33] the mill additions, and the firing conditions of the enamels used in this study. A typical two-frit, ground-coat enamel (No. 1) was used as the base coating for the test specimens; No. 2, a sign blue cover enamel, is a typical

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[24] H. Hecht and B. Oldenburg, "Standardization of Tests of Acid Resistance of Enamels," *Keram. Rundschau*, **43** [23] 263 (1935); *Ceram. Abs.*, **16** [6] 169 (1937).

[25] W. Dawihl, "Standardization of Testing Resistance of Vitreous Enamels Against Chemical Attack," *Chem. Fabrik*, **9**, 15–18 (1936); Enamel Bibliography, 1944 ed., p. 12.

[26] H. Hecht and H. Hornke, "Standardization of Tests of Antiacidic Enamels," *Keram. Rundschau*, **44** [9] 99–100 (1936); *Ceram. Abs.*, **16** [1] 10 (1937).

[27] J. E. Hansen, Manual of Porcelain Enameling, p. 244. Enamelist Publishing Co., Cleveland, Ohio, 1937; Enamel Bibliography, 1944 ed., p. 112.

[28] "Enamel Utensils, New South Wales Regulation," *Australian Food*, **7** [4] 19 (1937); Enamel Bibliography, 1944 ed., p. 79.

[29] K. P. Azarov and V. I. Savchenko, "Resistance of Enamel to Acid Under High Pressure," *Céram., Verrerie Émail*, **6** [2] 41–51 (1938); Enamel Bibliography, 1944 ed., p. 17.

[30] "Proposed British Standard Test for Acid Resistance," *Chem. Trade Jour.*, **105**, 424 (1939).

[31] Gerhard Schmidt, "Determination of Resistance to Acids of Enamels," *Glashütte*, **70** [25] 313–15 (1940); *Ceram. Abs.*, **20** [1] 8 (1941).

[32] F. A. Petersen and A. I. Andrews, "Enameled Utensil Manufacturers' Council Tentative Standard Solubility Test for Porcelain Enameled Cooking Utensils," *Jour. Amer. Ceram. Soc.*, **27** [4] 113–15 (1944).

[33] A. I. Andrews and R. L. Cook, Enamel Laboratory Manual. Garrard Press, Champaign, Ill., 1941; *Ceram. Abs.*, **21** [1] 7 (1942).

TABLE I

COMPOSITIONS USED IN STUDY OF CHEMICAL DURABILITY OF PORCELAIN ENAMELS

| | No. 1 Ground-coat frit | | No. 2 Sign blue cover | No. 3 Blue zirconium cover | No. 4 Chemical acidproof cover | No. 5 White cover | No. 6 White cover | No. 7 White cover | No. 8 White cover |
|---|---|---|---|---|---|---|---|---|---|
| | (A) | (B) | | | | Fluoride | Antimony | Zirconium | Acid-resistant |
| **Frit batch** | | | | | | | | | |
| Feldspar (Keystone) | 20.8 | 21.2 | 38.0 | 28.3 | | 27.0 | 17.6 | | 9.5 |
| Borax | 34.6 | 34.2 | 30.0 | 33.6 | | 28.0 | 22.9 | | 18.0 |
| Quartz | 27.7 | 21.5 | 16.0 | 6.1 | | 19.0 | 23.5 | | 39.0 |
| Soda ash | 4.6 | 5.6 | 4.0 | 7.0 | | 7.0 | 6.7 | | 10.0 |
| Soda niter | 4.7 | 4.7 | 3.0 | 4.0 | | 4.0 | 2.9 | 3.08 | 3.0 |
| Fluorspar | 5.1 | 10.3 | 3.0 | 7.0 | | 5.0 | 2.5 | 4.40 | 1.5 |
| Manganese dioxide | 1.5 | 1.5 | | 1.5 | | | | | |
| Cobalt oxide | 0.5 | 0.5 | 2.0 | 1.0 | | | | | |
| Nickel oxide | 0.5 | 0.5 | | | | | | | |
| Cryolite | | | 4.0 | | | 10.0 | 8.4 | 12.30 | |
| Zircon | | | | 12.0 | | | | 10.80 | |
| Zinc oxide | | | | | | | 2.9 | 4.40 | |
| Sodium antimonate | | | | | | | 12.6 | | 9.5 |
| Aluminum hydrate | | | | | | | | 3.96 | |
| Dehydrated borax | | | | | | | | 22.60 | |
| Calcite | | | | | | | | 7.74 | |
| Pyrophyllite | | | | | | | | 31.70 | |
| Sodium silicofluoride | | | | | | | | | 5.0 |
| Bone ash | | | | | | | | | 1.5 |
| Titanium dioxide | | | | | | | | | 3.0 |
| **Mill batch** | | | | | | | | | |
| Frit | 70 | 30 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Clay (Vallendar) | 7.5 | | | | | 6.0 | 6.0 | 6.0 | 5.0 |
| Florida kaolin | | | 6.0 | 6.0 | 1.0 | | | | |
| Borax | 0.75 | | | | | | | | |
| Magnesium carbonate | | | 0.25 | 0.25 | | 0.25 | 0.25 | 0.25 | |
| Bentonite | | | | | 0.25 | | | | 0.25 |
| Sodium aluminate | | | | | 0.25 | | | | 0.25 |
| Barium chloride | | | | | 0.10 | | | | |
| Tin oxide | | | | | | 6.0 | | | 5.0 |
| Treopax | | | | | | | 2.0 | 2.0 | |
| Water | 45 | | 40 | 40 | 46 | 40 | 40 | 40 | 38 |
| **Firing conditions** | | | | | | | | | |
| Temp. (°F.) | 1575 | | 1500 | 1520 | 1520 | 1460 | 1500 | 1460 | 1530 |
| Time (minutes) | 5 | | 3 | 5 | 3 | 2½ | 2½ | 2½ | 3 |

weather-resistant composition used extensively on porcelain enameled signs; No. 3, a blue zirconium cover enamel, which is a special type particularly resistant to the attack of distilled water in the autoclave test; No. 4, an enamel used extensively in the chemical-process industries for coating tanks, digesters, large evaporators, autoclaves, and other similar equipment; No. 5, a fluoride enamel which contains a relatively high content of fluorspar and cryolite; No. 6, a super-opaque antimony enamel in which most of the opacifier is smelted into the frit; No. 7, one of the recently developed antimony-free or zirconium enamels which also develops a high degree of opacity; and No. 8, an acid-resistant, white cover enamel.

The two ground-coat enamel frits, the fluoride cover, the antimony cover, and the acid-resistant white cover enamels were smelted in 50-lb. batches in a rotary smelter. Several 5-lb. batches of each of the other three compositions, the sign blue cover, the blue zirconium cover, and the zirconium white cover enamels, were smelted in crucible smelters and thoroughly mixed to form composite samples.

The ground-coat enamel was milled to a fineness of 8 to 10% and the covers to 6 to 8% on a No. 200 sieve, using the Standard Method for Fineness.[34]

## (2) Selection and Preparation of Test Specimens

It was felt that the test sample should be of such shape that it could form the container in which the chemical solution was placed and also that it be of such size and weight that it could be accurately weighed on an analytical balance; further, both horizontal and vertical surfaces of the test specimen should be exposed to the attack of the test solutions. Shallow-drawn cylindrical enameling iron shapes, 2.50 in. in diameter and 1.75 in. in depth with a flange 0.625 in. around the top, were chosen as best meeting these conditions.

The test cups were properly cleaned in boiling alkaline cleaner at a concentration of 8 oz. per gallon, rinsed in hot water, pickled in an 8% solution of sulfuric acid at 160°F., rinsed in hot water, neutralized in a solution

[34] A. I. Andrews, Enamels. Twin City Printing Co., Champaign, Ill., 1935; Enamel Bibliography, 1944 ed., p. 12.

containing 0.10% $Na_2O$ added as sodium cyanide, and dried. The ground-coat enamel was applied over the entire surface of the container by slushing; the test cups were dried and fired at 1575°F. for 5 minutes. The test cups used to study the ground-coat surface were given a second ground-coat application to assure adequate coverage of the metal base.

In general, two separate coats of each cover enamel were applied and fired on the ground-coated containers. In the preparation of the acid-resistant white enamel surfaces, the antimony white enamel was applied directly on the ground coat and fired; then the acid-resistant white enamel was applied as a second coat and fired. The test cups which appeared satisfactory were further tested by the Cesco spark tester.* This instrument is held approximately $^1/_4$ to $^1/_2$ in. above the enamel surface and moved progressively over the surface to be tested. If there is an imperfection in the enamel coating, due either to a break in the surface or to an air bubble just below the enamel surface, a concentration of the discharge spark is evident. Only those samples which showed no surface imperfections were used in determining the chemical attack of the various test solutions.

### (3) Chemical Solutions

In the selection of chemical solutions to be used in the study of the chemical durability of the various porcelain enamel surfaces, it was desired to obtain a comprehensive coverage of the inorganic and organic acids and alkalis and of many of the representative salts. Insofar as possible and desirable, the comparative attacks at both room and boiling temperatures were determined. The following general procedure was used in testing the various enamel surfaces: The effect of the chemical solutions at room temperature was tried; where the degree of attack was appreciable, the loss in weight was determined at time intervals of 1, $2^1/_2$, 5, 10, 20, 40, 80, and 180 hours or until a failure occurred in the surface. In cases where the total loss of weight at room temperature was low, determinations were made at boiling temperatures at time intervals of 10, 25, 50, and 100 hours.

The chemical solutions used and their concentration expressed as the percentage and as normality are given in Table II. They were prepared from either c.p. or U.S.P. chemicals, and, in general, can be divided into four main groups, the inorganic acids, the organic acids, the alkalis, and the salts. The organic acid solutions were prepared just before they were used to minimize the effect of possible subsequent decomposition.

### (4) Method of Test

The representative porcelain enameled test cups, which showed a satisfactory nonconducting surface, were carefully weighed on an analytical balance to the nearest 0.0001 gm.; 100 cc. of the test solution were measured and poured into the enameled container. A watch glass was placed on top of the container to prevent contamination and to minimize evaporation losses. After the test solution was allowed to remain in contact with the enamel surface for the stated time interval, the solution was poured into a 100-cc. Pyrex-brand graduate, the container rinsed with distilled water, dried in an electric oven at 200°F., and, after cooling to room temperature, reweighed, and the solution then was returned to the container. This procedure was repeated at the stated time intervals until the test surface was attacked to such a degree that the under surface showed through. With the white enamel surfaces, this attack was readily discernible, but with the blue cover enamels or the ground coat, particularly when an appreciable amount of etching or attack had taken place, it was difficult to distinguish a surface failure. With this latter type of surface, the RCA, Jr.,

* The Cesco tester is a high-voltage discharge spark cell manufactured by the Chicago Electric Scientific Co.

TABLE II

CHEMICAL SOLUTIONS USED

| Chemical material | Chemical formula | Concentration (%) | Normality (%) |
|---|---|---|---|
| **Group I: Inorganic acids** | | | |
| Hydrochloric | HCl | 35 | 9.60 |
| | | 20 | 5.50 |
| | | 10 | 2.75 |
| | | 1 | 0.27 |
| Sulfuric | $H_2SO_4$ | 98 | 20.00 |
| | | 60 | 12.25 |
| | | 25 | 5.10 |
| | | 10 | 2.04 |
| | | 1 | 0.20 |
| Nitric | $HNO_3$ | 70 | 11.10 |
| | | 20 | 3.17 |
| | | 10 | 1.58 |
| | | 1 | 0.16 |
| Phosphoric | $H_3PO_4$ | 85 | 26.00 |
| | | 20 | 6.12 |
| | | 10 | 3.06 |
| | | 1 | 0.31 |
| **Group II: Organic acids** | | | |
| Acetic | $H_4C_2O_2$ | 10 | 1.67 |
| Citric | $H_8C_6O_7$ | 10 | 1.56 |
| Tartaric | $H_6C_4O_6$ | 10 | 1.33 |
| Lactic | $H_6C_3O_3$ | 10 | 1.11 |
| Malic | $H_6C_4O_5$ | 10 | 1.49 |
| Oxalic | $H_2C_2O_4$ | 10 | 2.22 |
| Pyrogallic | $H_6C_6O_3$ | 10 | 2.38 |
| Carbolic | $C_6H_5OH$ | 10 | 1.06 |
| **Group III: Alkalis** | | | |
| Sodium hydroxide | NaOH | 10 | 2.50 |
| **Group IV: Selected salts** | | | |
| Sodium chloride | NaCl | 10 | |
| Sodium carbonate | $Na_2CO_3$ | 10 | |
| Sodium borate | $Na_2B_4O_7$ | 10 | |
| Sodium bicarbonate | $NaHCO_3$ | 10 | |
| Magnesium sulfate | $MgSO_4$ | 10 | |
| Sodium sulfate | $Na_2SO_4$ | 10 | |
| Sodium sulfite | $Na_2SO_3$ | 10 | |
| Trisodium phosphate | $Na_3PO_4$ | 10 | |
| Disodium acid phosphate | $Na_2HPO_4$ | 10 | |
| Sodium nitrate | $NaNO_3$ | 10 | |
| Zinc chloride | $ZnCl_2$ | 10 | |
| Aluminum chloride | $AlCl_3$ | 10 | |

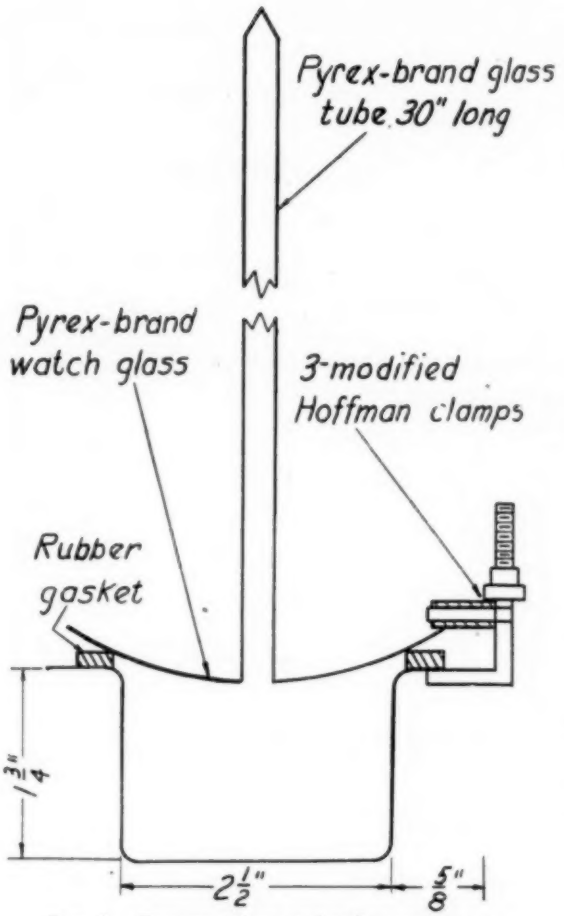


FIG. 1.—Test container and reflux condenser.

Volt-Ohmyst was used to measure the comparative electrical resistance of the enamel surface. If the electrical resistance showed a decided drop, a failure in the enamel surface was indicated.

The enamel surfaces, which were not attacked appreciably at room temperature, were further checked at boiling temperatures. In studying the attack of the boiling chemical solutions on the porcelain enameled containers, simple equipment was desired so that many samples could be run at the same time. A simple type of reflux condenser was found to be most satisfactory. As illustrated in Fig. 1, a straight 10-mm. Pyrex-brand glass tube, 30 in. long, was sealed to the center of a Pyrex-brand watch glass, 90 mm. in diameter. A rubber gasket was placed on the container and the glass reflux condenser was clamped firmly in place by three modified L-shaped Hoffman clamps.

In heating the samples at boiling temperatures, a regular 3000-watt, Hevi-Duty electric hot plate was used. A rheostat was connected in series with the electric hot plate and adjusted to give a plate temperature of 260°F. when measured with a Pyrocon surface pyrometer. When the electric hot plate was operating at this temperature, vigorous boiling action was obtained.

The method of determining the rate of attack at boiling temperatures was the same as that used at room temperatures.

The surface area exposed to chemical action, with exactly 100 cc. of solution in the test containers, was found to average 15.58 sq. in. with a variation of less than 1.5%. The average ratio of the horizontal to the vertical surface areas for these containers was about 1 to 2.

## IV. Results and Discussion

The porcelain enamel surfaces were exposed to the chemical action of the various solutions which were measured into the weighed test containers. After standing for definite time intervals, the loss in weight expressed in grams per square inch was determined for each different test condition. The comparative effects of the inorganic and organic acids, the alkalis, and the selected salts were investigated at room or at boiling temperatures and, in some cases, at both room and boiling temperatures.

### (1) Chemical Durability at Room Temperature

The resistance of the various selected porcelain enamel surfaces to the attack of the different chemical solutions at room temperature was determined.

(*A*) *Effects of Inorganic Acids:* The comparative effects of the various concentrations of the four inorganic mineral acids on the selected porcelain enamel surfaces are presented in Figs. 2 to 8. The curves show the loss in weight expressed as milligrams per square inch as plotted against time in hours. It is to be noted particularly that a change of scale occurs at the 40-hour time period.

(i) *Ground-Coat Enamels:* In Fig. 2 ((*A*), (*B*), (*C*), and (*D*)), the effects of different concentrations of hydrochloric, sulfuric, phosphoric, and nitric acids, respectively, on the ground-coat surfaces are plotted.

Figure 2 (*A*) indicates that the concentrated hydrochloric acid showed little initial attack over the first 40 hours, but thereafter the rate of attack increased rapidly. With both the 20% and 10% solutions, the rate of attack was very high, breaking through the ground-coat surface after 10 hours. The 1% solution showed a moderate rate of attack over the first 40 hours and then leveled off with no further attack. Two factors which might explain the action of the 1% solution are (1) that the strength of the acid was depleted so no further action could take place and (2) that the products formed as a result of the action of the acid on the enamel surface decreased further attack.

In Fig. 2 (*B*), the effect of the different concentrations of sulfuric acid is given. The concentrated acid showed practically no attack; the 60% acid showed slightly increasing attack for the first 40 hours, then a sharp increase between 40 and 80 hours, finally breaking through the enamel surface in a small spot due to localized corrosion after the 80-hour period. The 25% solution attacked the ground-coat enamel rapidly and broke through the surface after 10 hours. With the 10% acid, the initial rate of attack was about the same as that of the 25% acid; after 5 hours, the rate of attack

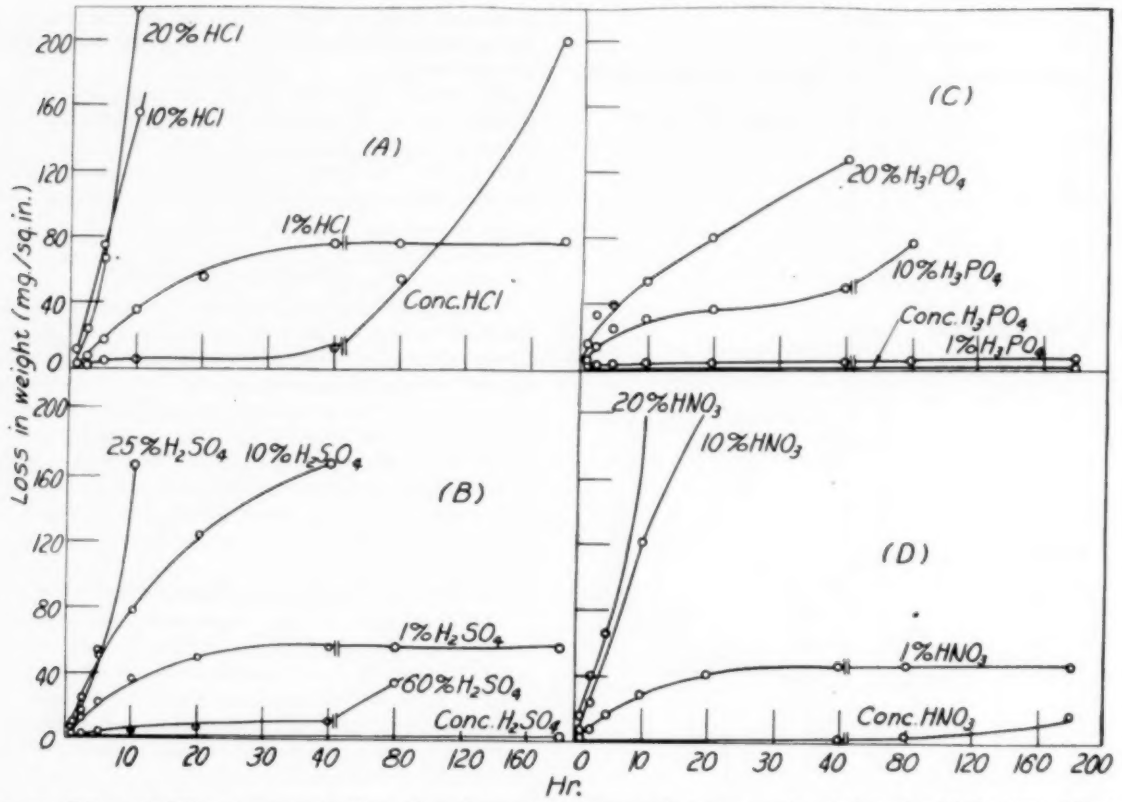


FIG. 2.—Effect of different concentrations of various acids on ground-coat enamels: (*A*) hydrochloric, (*B*) sulfuric, (*C*) phosphoric, and (*D*) nitric.

decreased and the curve started to flatten out at the 40-hour period but broke through the surface on the 80-hour period. With the 1% solution, the acid attack increased moderately to 40 hours and then leveled off, showing no further attack even after 180 hours.

Figure 2 (*C*) shows the effect of different concentrations of phosphoric acid. The concentrated acid showed practically no attack; the 20% solution showed a moderate attack breaking through the enamel surface after 40 hours; the 10% acid showed less total attack than the 20% but broke through the surface after 80 hours; and the 1% solution showed a slight amount of chemical attack.

In Fig. 2 (*D*), the effect of different concentrations of nitric acid is given. The concentrated acid showed a slight amount of attack in 40 hours and an increasing amount thereafter; the 20% acid showed a rapid attack, breaking through the ground-coat enamel surface in 10 hours; the 10% solution also showed rapid attack but not as high as the 20% solution, the enamel coating being eaten through in 20 hours; and the 1% solution showed a moderate amount of attack to 40 hours but very little thereafter.

In comparing the effect of the four strong mineral acids on the ground coats, the concentrated acids, except the hydrochloric acid, showed slight attack, while the 10% and 20% or 25% acids showed sufficient attack to break through the surface in a comparatively short time. With the 1% solutions, the acids showed varying amounts of total attack in the order of hydrochloric, sulfuric, nitric, and phosphoric acids. With the first three acids, the degree of total attack of the 1% acids was proportional to the normality of the solutions, while the degree of attack with the phosphoric acid was still increasing after the 180-hour period.

(ii) *Fluoride White Cover Enamels:* In Fig. 3 ((*A*), (*B*), (*C*), and (*D*)), the effect of different concentrations of the mineral acids on fluoride white cover enamel surfaces is plotted.

Figure 3 (*A*) shows that the concentrated hydrochloric acid attacked this surface rapidly, the enamel being removed in 10 hours; the 20% acid attacked the surface rapidly, the enamel being removed in 5 hours; the 10% acid attacked the fluoride surface almost as rapidly as the 20% acid, breaking through the surface in 5 hours; and the 1% acid showed considerable attack in the first 5 hours, followed then by a slight increase to the 180-hour period.

In Fig. 3 (*B*), the effect of the different concentrations of sulfuric acid is given. The concentrated acid showed practically no attack; and the 60% acid, moderate attack, breaking through the surface in a localized area after 20 hours. The 25% acid showed a fairly rapid attack, removing the fluoride white coating in 10 hours. The 10% acid showed the most rapid attack of the various concentrations, although there was not a sufficient amount of enamel removed to show the ground coat until after the 20-hour period. The 1%

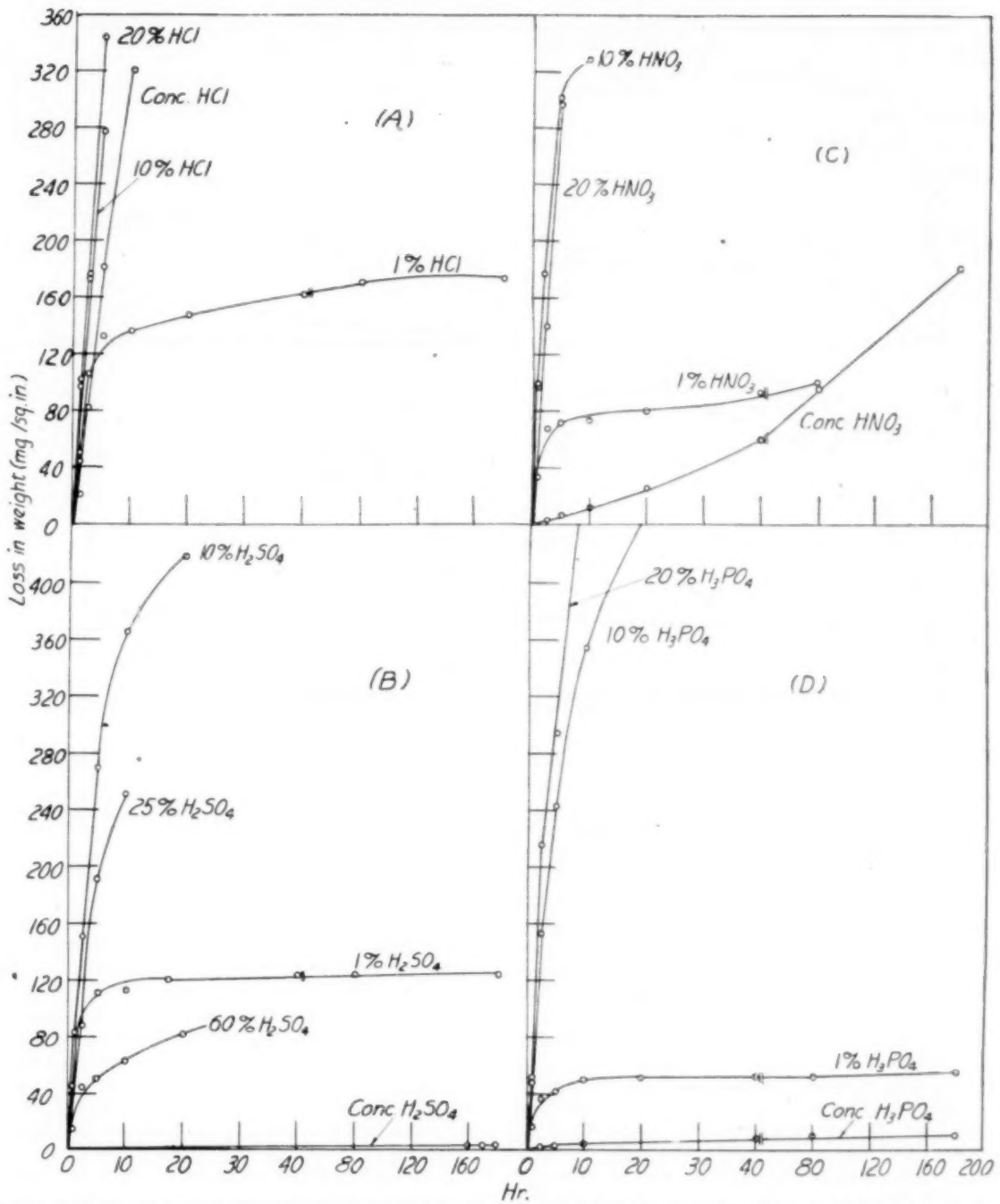


FIG. 3.—Effect of different concentrations of various acids on fluoride white cover enamels: (*A*) hydrochloric, (*B*) sulfuric, (*C*) nitric, and (*D*) phosphoric.

acid showed a fairly rapid initial attack in the first 5 hours, then practically leveled off with slight additional chemical attack.

The effect of the different concentrations of nitric acid is given in Fig. 3 (*C*). The concentrated acid showed increasing attack with time, although the surface was not broken through after 180 hours. The 20% acid showed rapid attack, the enamel being removed sufficiently to show the ground coat in 5 hours; the 10% acid showed slightly greater attack than the 20% solution, but the curve began to flatten and the surface was not broken through until the 10-hour period; while the 1% solution showed a moderate attack in the first 5 hours and then slightly increasing attack until it broke through the surface after the 80-hour period.

The group of curves showing the effect of the differ-

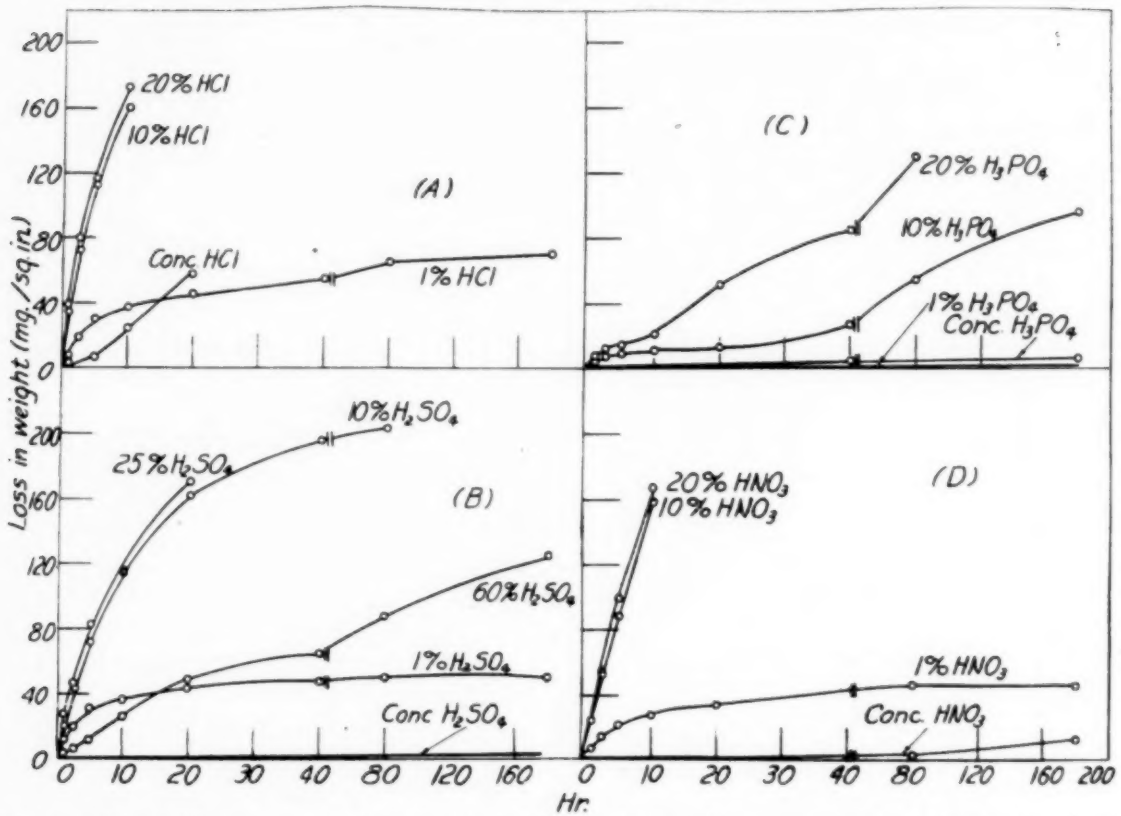


FIG. 4.—Effect of different concentrations of various acids on antimony white cover enamels: (*A*) hydrochloric, (*B*) sulfuric, (*C*) phosphoric, and (*D*) nitric.

ent concentrations of phosphoric acid on the fluoride enamel surfaces is given in Fig. 3 (*D*). The concentrated acid showed a slight amount of surface attack; the 20% solution, very rapid attack, breaking through the surface after the 20-hour period; the 10% phosphoric acid, slightly lower attack than the 20% solution but did not break through even after 180 hours; and the 1% solution, relatively low attack in the first 10 hours and practically none thereafter.

In comparing the attack of the four strong mineral acids on the fluoride white cover enamels, the total solubility is considerably greater than with the groundcoat enamel. With the concentrated acids, the phosphoric acid showed slightly greater attack than the sulfuric acid; the nitric acid, a moderate degree of attack; and the hydrochloric acid, pronounced attack. The 10% and 20% or 25% solutions of the different acids showed decided attack, and the 1% solutions, an appreciable initial attack with very slight increase thereafter.

(iii) *Antimony White Cover Enamel:* In Fig. 4 ((*A*), (*B*), (*C*), and (*D*)), the effects of different concentrations of the mineral acids on the antimony white cover enamels are shown.

The effect of different concentrations of hydrochloric acid is plotted in Fig. 4 (*A*). The concentrated solution showed increasing attack with time and broke through the enamel surface after 20 hours; both the 10% and 20% solutions showed comparatively rapid attack, breaking through the surface after 10 hours in each case, and the 1% solution showed progressively increasing attack even after 180 hours.

In Fig. 4 (*B*), the effect of different concentrations of sulfuric acid is shown. The concentrated acid showed practically no attack, while with the 60% acid, there was progressively increasing attack; the 25% solution showed the greatest attack of this group, breaking through the surface in 20 hours. A 10% solution showed slightly less attack than the 25% solution, breaking through the surface in 80 hours, while the 1% solution showed a more rapid initial rate of attack than the 60% solution but practically no further attack after 40 hours.

In the series of curves shown in Fig. 4 (*C*), the effects of different concentrations of phosphoric acid on the antimony cover enamel are plotted. The concentrated acid showed very slight attack; the 20% acid, an increasing degree of attack after 10 hours and broke through the surface after 80 hours; the 10% acid, a low rate of attack for 40 hours and then a sharply increasing amount of attack through the 180-hour period; and the 1% solution, less attack than that of the concentrated solution of phosphoric acid.

In Fig. 4 (*D*), the effects of different concentrations of nitric acid are given. The antimony enamel showed an initial resistance to the attack of the concentrated

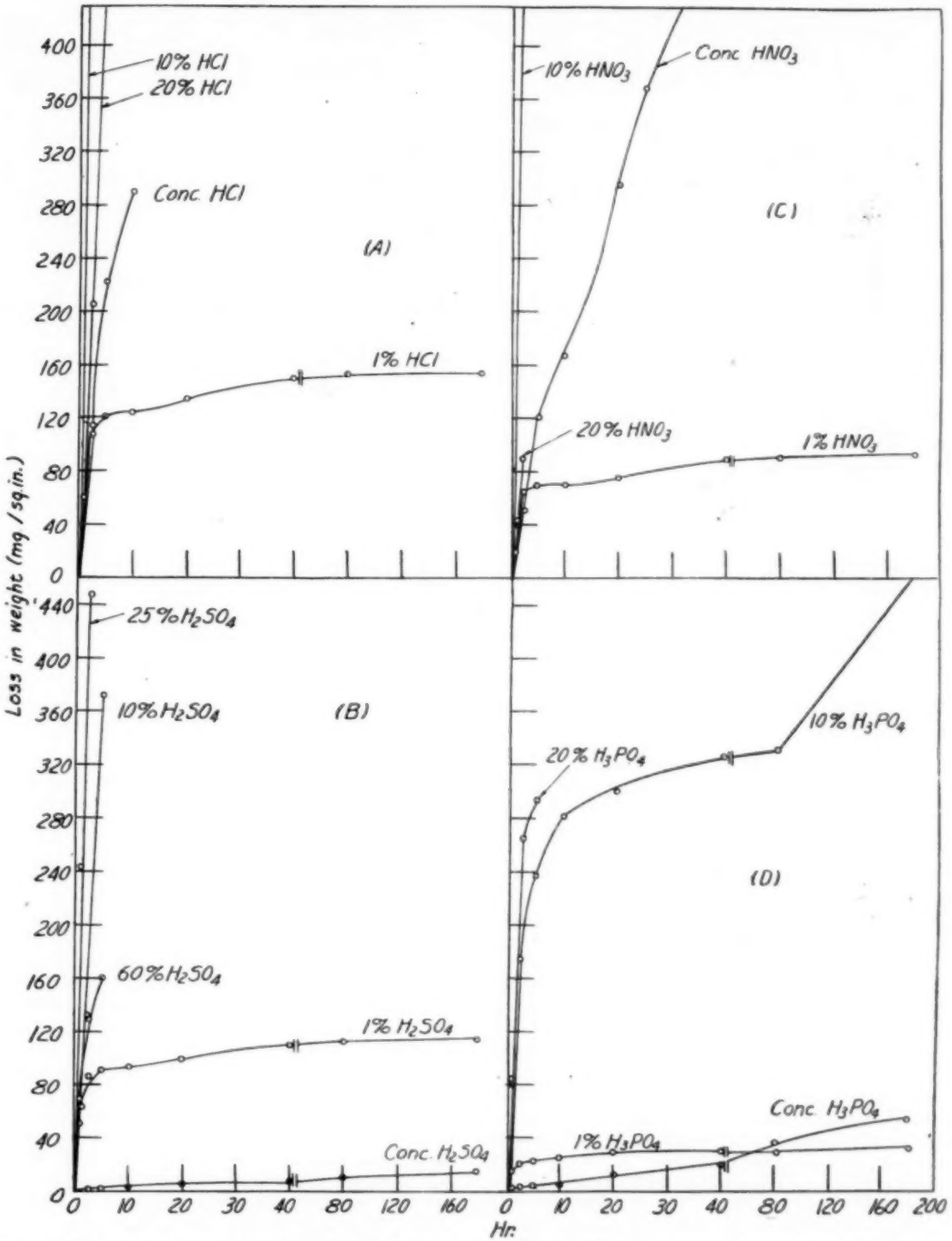


FIG. 5.—Effect of different concentrations of various acids on zirconium white cover enamels: (*A*) hydrochloric, (*B*) sulfuric, (*C*) nitric, and (*D*) phosphoric.

acid, but the curve was starting to rise after the 180-hour period; the 10% and 20% solutions showed about the same rate of attack, with both breaking through the surface after 10 hours; and the 1% solution, a moderately increasing attack.

In summarizing the effects of the different mineral

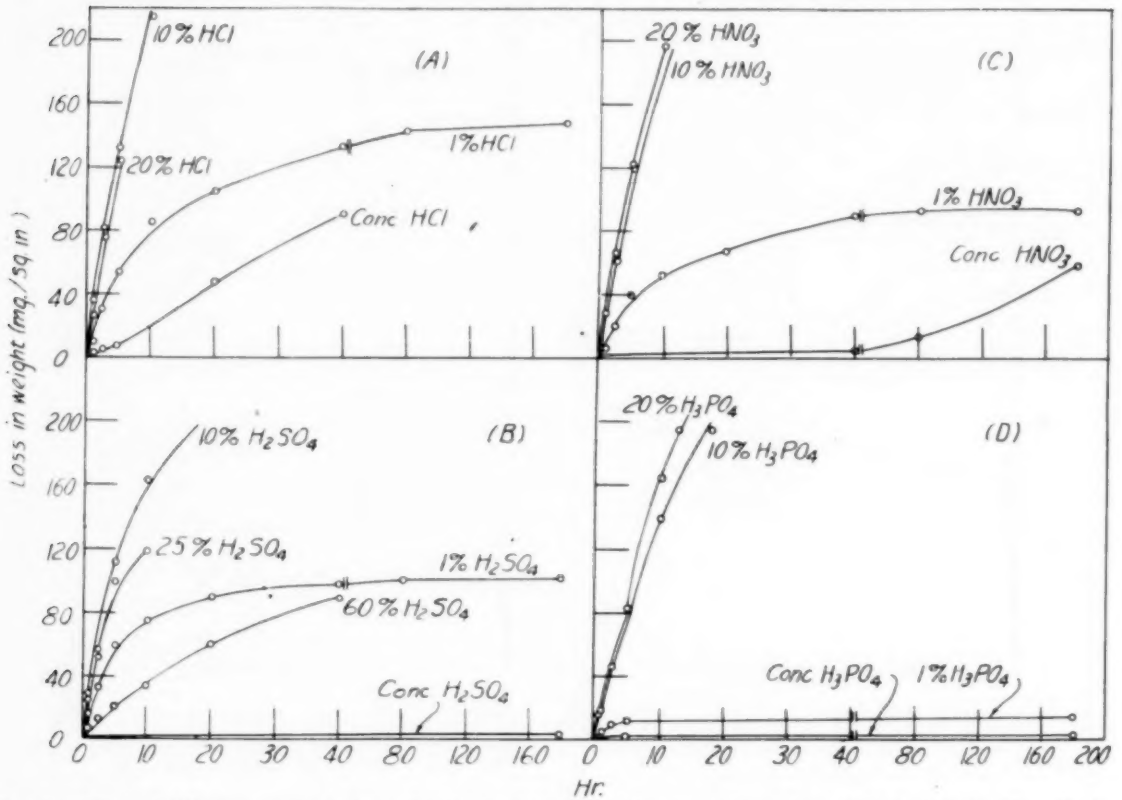


FIG. 6.—Effect of different concentrations of various acids on sign blue cover enamels: (*A*) hydrochloric, (*B*) sulfuric, (*C*) nitric, and (*D*) phosphoric.

acids on the antimony cover enamels, the total degree of attack is obviously much less than that of the fluoride cover enamel. Of the concentrated acid solutions, only hydrochloric acid showed pronounced attack. The nitric acid began to show increasing attack after 180 hours, while both the sulfuric and phosphoric acids showed very slight total attack. With the 10% and 20% or 25% solutions of hydrochloric, nitric, and sulfuric acids, there was pronounced attack, while the attack with phosphoric acid was much less and the difference between the attack of the 10% and 20% solutions was greater. The 1% hydrochloric, nitric, and sulfuric acids showed similar curves, varying only in the degree of total attack, while the 1% solution of phosphoric acid showed very slight attack.

(iv) *Zirconium White Cover Enamel:* In Fig. 5 ((*A*), (*B*), (*C*), and (*D*)), the effects of different concentrations of the strong mineral acids on zirconium white cover enamel surfaces were plotted.

In Fig. 5 (*A*), the effect of different concentrations of hydrochloric acid is given. The concentrated acid showed considerable attack, breaking through after 10 hours; both the 10% and 20% solutions showed extremely rapid attack; and the 1% solution, high initial attack for 5 hours and then only slightly increasing chemical attack.

The effect of the different concentrations of sulfuric acid is shown in Fig. 5 (*B*). The concentrated acid showed some attack on this surface and the 60% acid showed considerable attack, breaking through the surface in 5 hours. The 25% solution showed very pronounced attack, breaking through the surface in $2^1/_2$ hours; the 10% solution of sulfuric acid, considerable attack, breaking through the surface in 5 hours; and the 1% solution, rapid attack for the first $2^1/_2$ hours, slightly increasing thereafter.

In Fig. 5 (*C*), the effect of the different concentrations of nitric acid is given. The concentrated acid showed a high amount of attack on the zirconium enamel and the 20% acid, considerable attack, breaking through in $2^1/_2$ hours. The 10% solution showed very rapid and high total attack, breaking through the surface in $2^1/_2$ hours; while the 1% acid showed considerable attack for the first $2^1/_2$ hours with only a slight increase thereafter.

In Fig. 5 (*D*), the effect of the different concentrations of phosphoric acid on a zirconium white cover enamel was plotted. The concentrated acid showed a fair degree of chemical attack which increased almost linearly with time, and the 20% acid showed rapid attack, breaking through the surface after 5 hours. Almost as much chemical attack was shown by the 10% solution as by the 20% solution in the initial 5 hours, but thereafter the curve began to flatten and although showing a high amount of total attack did not break through the surface in 180 hours. The initial rate of attack of the 1% solution was greater than that of the concentrated acid but the degree of total chemical

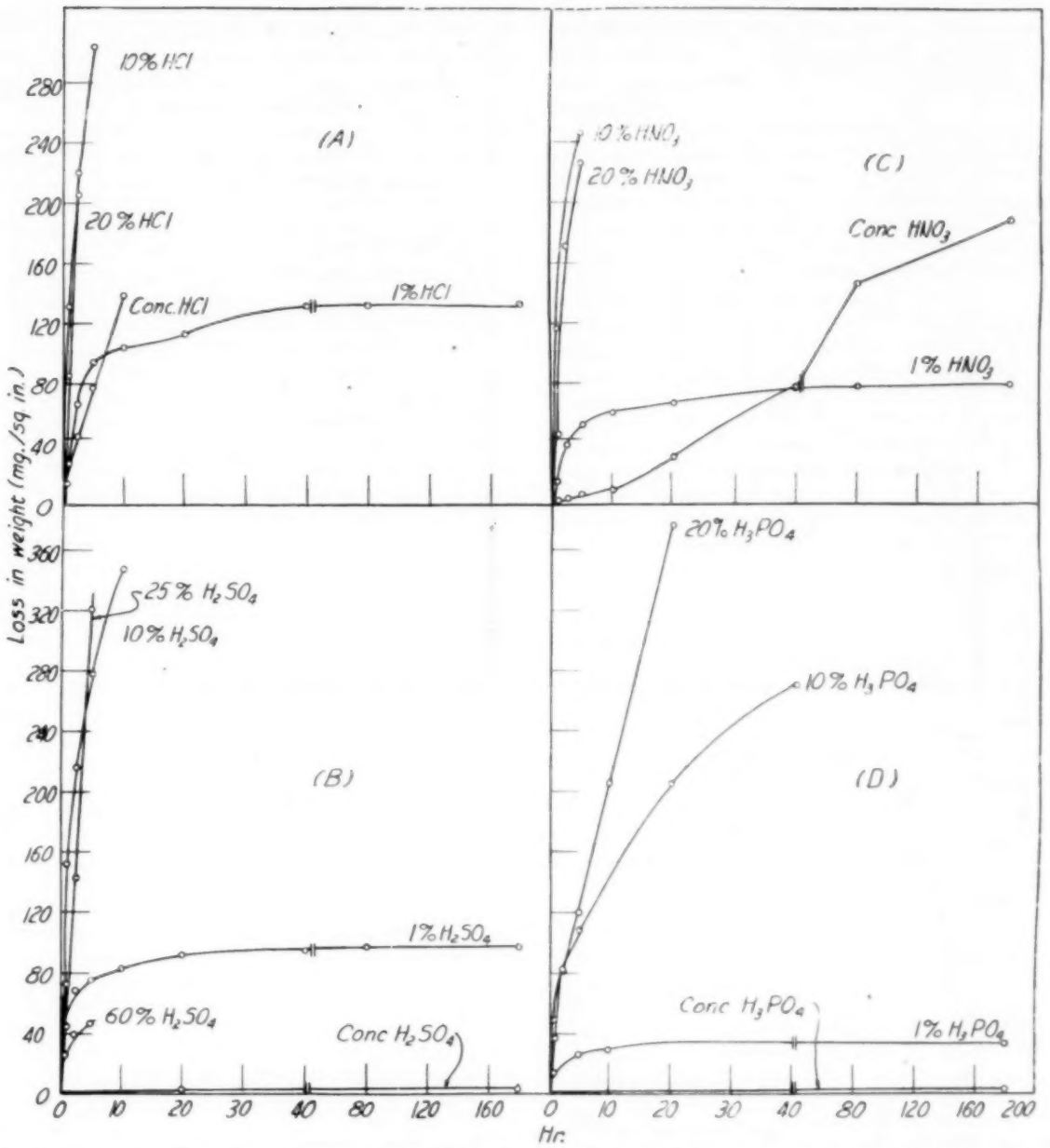


FIG. 7.—Effect of different concentrations of various acids on blue zirconium cover enamels: (*A*) hydrochloric, (*B*) sulfuric, (*C*) nitric, and (*D*) phosphoric.

attack was less than that of the concentrated acid over the 180 hours.

In comparing the effects of the four mineral acids on the zirconium white cover enamels, it is apparent that the degree of chemical attack is very high, being comparable to or greater than that shown by the fluoride cover enamel surfaces. With the concentrated acids, the sulfuric acid showed the least attack; the phosphoric acid, slightly greater; while the hydrochloric and nitric acids showed considerable attack. In every case, the 10% and 20% or 25% solutions showed a high amount of attack while the 1% solutions showed characteristics similar to those for the other enamel surfaces.

(v) *Sign Blue Cover Enamel:* The effects of different concentrations of the four strong mineral acids on the sign blue cover enamel are shown in Fig. 6 ((*A*), (*B*), (*C*), and (*D*)).

In Fig. 6 (*A*), the effect of different concentrations of hydrochloric acid is given. The concentrated acid showed increasing attack, breaking through the surface after 40 hours; the 20% acid showed rapid attack, breaking through the surface in 5 hours; the 10% solution showed slightly greater attack than the 20%

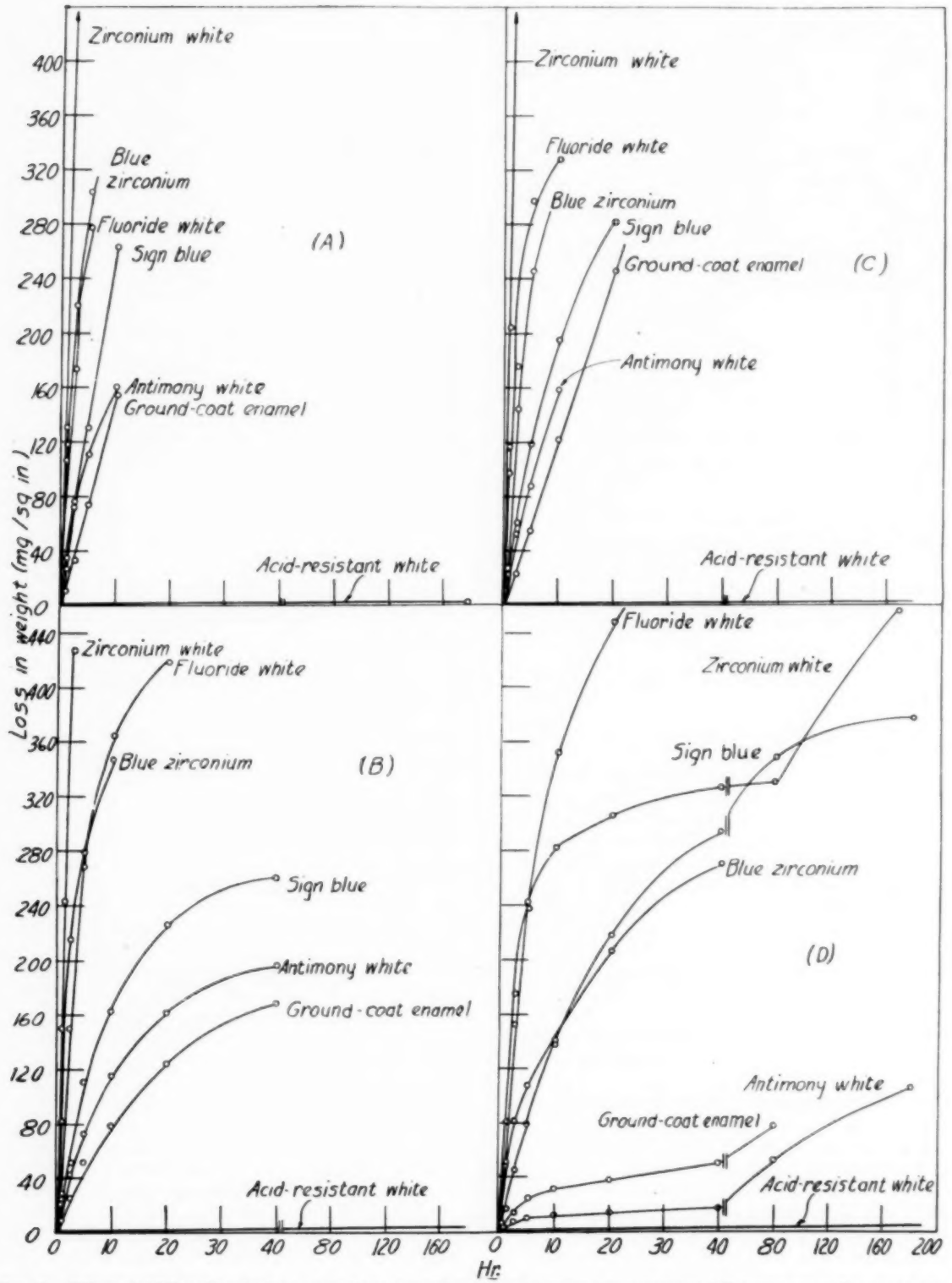


FIG. 8.—Effect of 10% acid solutions on various enamel surfaces at room temperatures (all cover enamels except one ground coat): (*A*) hydrochloric, (*B*) sulfuric, (*C*) nitric, and (*D*) phosphoric.

acid but did not expose the under surface until after 10 hours. The 1% solution showed moderately increasing attack to the 80-hour period with only a slight increase for the total 180 hours.

The effect of different concentrations of sulfuric acid is shown in Fig. 6 (*B*). The concentrated acid showed very slight attack; the 60% acid, moderate attack, breaking through after 40 hours; and the 25% acid, fairly rapid attack, breaking through the surface after 10 hours. The 10% solution showed slightly greater attack than the 25% acid, rupturing the surface after 40 hours; while the 1% solution showed moderate attack over the 40 hours with only a slight increase afterward.

In Fig. 6 (*C*), the effect of different concentrations of nitric acid is given. The concentrated acid showed only slight attack for the first 40 hours, but the curve started to rise appreciably thereafter. The 20% and 10% solutions showed rather rapid attack, breaking through the surface after 10 and 20 hours, respectively, and the 1% solution showed moderately increasing attack over the first 40 hours and only a slight amount thereafter.

Figure 6 (*D*) shows the effect of different concentrations of phosphoric acid on the sign blue cover enamel. The concentrated acid showed only slight attack, but the 20% acid showed a considerable amount, breaking through the surface after 40 hours. The 10% solution showed about the same initial rate of attack as the 20% solution, but the surface was not broken through even after 180 hours, and the 1% solution showed slightly greater surface attack than the concentrated acid.

In summarizing the effects of the mineral acids on the sign blue cover enamel, this enamel is, in general, more resistant to acid attack than either the fluoride or zirconium cover enamels and about comparable to the ground-coat or antimony cover enamels. With the concentrated acids, only hydrochloric acid showed marked attack; the nitric acid began to show some attack after 80 hours; while the sulfuric and phosphoric acids showed practically no attack. The intermediate concentrations showed a fair amount of attack, while the 1% solution showed slight-to-moderate amount of total attack.

(vi) *Blue Zirconium Cover Enamel:* In Fig. 7 ((*A*), (*B*), (*C*), and (*D*)), the effects of different concentrations of the four mineral acids on blue zirconium cover enamel are given.

In Fig. 7 (*A*), the effect of different concentrations of hydrochloric acid is shown. The concentrated acid showed rather rapid attack, the surface being broken after 10 hours; the 20% acid showed rapid attack, breaking through the surface after $2^1/_2$ hours. The 10% solution also showed rapid chemical attack, the surface being broken after 5 hours; and the 1% solution exhibited appreciable attack during the first 5 hours but very little thereafter.

In Fig. 7 (*B*), the effect of different concentrations of sulfuric acid is shown. The concentrated acid showed essentially no attack; the 60% acid showed very little total attack, but due to localized corrosion broke through the surface after 5 hours. The 25% solution showed rapid attack, breaking through the surface after 5 hours; the 10% solution also showed rapid chemical attack, breaking through the surface in 10 hours; and the 1% acid, a moderate increase for 10 hours, then practically no further attack in the 180-hour period.

In Fig. 7 (*C*), the effect of different concentrations of nitric acid is given. The concentrated acid showed little attack for the first 10 hours but rapidly increasing attack from then on through the 180-hour period. The 10% and 20% solutions showed rapid attack, breaking through the surface after 5 hours; and the 1% solution, moderately increasing attack for the first 20 hours, then only slight additional attack.

Figure 7 (*D*) shows the effect of different concentrations of phosphoric acid. The concentrated acid showed practically no attack while the 20% acid exhibited considerable attack, breaking through the surface after 20 hours; the 10% solution, a fair amount of chemical attack, breaking through the surface after 40 hours; and the 1% acid solution, slight attack.

In summarizing the effect of the mineral acids on blue zirconium cover enamel, this enamel, in general, is much less resistant to acid attack than either the regular ground-coat or the sign blue cover enamels. With the concentrated acids, both hydrochloric and nitric acids showed considerable attack, while sulfuric and phosphoric acids exhibited essentially no attack. In every case, the intermediate concentrations showed a considerable amount of chemical attack and the 1% solutions, a fair amount.

(vii) *Acid-Resistant White Cover Enamel:* The various concentrations of the four mineral acids showed very slight attack on these enamels at room temperature. None of these surfaces, after exposure to the attack of the mineral acids for 180 hours, showed a loss in weight above 0.001 gm. per sq. in.

(viii) *Comparison of Various Enamel Surfaces:* From an analysis of the previous curves, in general, the 10% acid solutions showed as rapid chemical attack as any of the solutions. In order to obtain a better visual picture of the comparative resistance of the various surfaces to acid attack, the effects of the 10% solutions of hydrochloric, sulfuric, nitric, and phosphoric acids on various enamel surfaces were plotted in Fig. 8 ((*A*), (*B*), (*C*), and (*D*)).

The effect of a 10% solution of hydrochloric acid is shown in Fig. 8 (*A*). The acid-resistant white enamel is the only surface capable of withstanding the 10% solution for longer than 10 hours. Of the other surfaces, the ground coat showed less total attack and a lower rate. In considering the white cover enamels, the antimony wnite was the most resistant; the fluoride white cover showed considerable attack; and the zirconium white cover was attacked very rapidly. The blue zirconium cover enamel showed about the same degree of attack as the fluoride white cover, while the sign blue cover showed attack intermediate between the antimony white and fluoride white cover enamels.

In Fig. 8 (*B*), the effect of 10% sulfuric acid is shown. The acid-resistant white cover enamel showed practically no attack. The ground-coat enamel was more resistant to attack than the antimony cover, and the

TABLE III

EFFECT OF FRESH SAMPLE OF SOLUTION FOR EACH TIME PERIOD

| Concentration and solution (%) | | Cumulative time (hr.) Loss in weight (gm./sq. in.) 1 | 2½ | 5 | 10 | 20 | 40 | 80 | 180 |
|---|---|---|---|---|---|---|---|---|---|
| | | Fluoride white cover enamel | | | | | | | |
| 1 | HCl | 0.0534 | 0.1408 | 0.2520 | 0.3810 | 0.4840 | * | | |
| 1 | $H_2SO_4$ | .0467 | .1203 | .2100 | .3140 | .4230 | * | | |
| 1 | $HNO_3$ | .0322 | .0863 | .1510 | .2315 | .3250 | 0.3990 | * | |
| 1 | $H_3PO_4$ | .0174 | .0444 | .0910 | .1323 | .1892 | .2440 | * | |
| 10 | HCl | .1095 | .1835 | .3860 | * | | | | |
| 10 | $H_2SO_4$ | .0861 | .1535 | .2680 | * | | | | |
| | | Antimony white cover enamel | | | | | | | |
| 1 | HCl | 0.0096 | 0.0215 | 0.0391 | 0.0629 | 0.0922 | 0.1290 | 0.1710 | * |
| 1 | $H_2SO_4$ | .0108 | .0238 | .0412 | .0642 | .0931 | .1260 | .1800 | * |
| 1 | $HNO_3$ | .0058 | .0130 | .0265 | .0399 | .0547 | .0645 | | |
| 1 | $H_3PO_4$ | .0016 | .0018 | .0019 | .0019 | .0020 | .0021 | | |
| 10 | HCl | .0351 | .0720 | .1323 | .1950 | * | | | |
| 10 | $H_2SO_4$ | .0228 | .0506 | .0950 | .1370 | .1940 | * | | |

* Indicates break in the enamel surface.

sign blue cover showed slightly greater attack than the antimony cover. Of the other three surfaces, the zirconium white cover showed very rapid attack, and the fluoride white as well as the blue zirconium cover enamels showed almost as high a degree of attack.

In Fig. 8 (*C*), the effect of a 10% solution of nitric acid is given. The acid-resistant white enamel was very resistant to attack, but the other surfaces were not very resistant to the attack of the 10% acid. The ground coat showed the lowest rate of attack; the antimony white cover and the sign blue cover, a slightly greater amount; the blue zirconium cover and white fluoride cover enamels, an appreciable rate; while the white zirconium cover, very rapid attack.

The effect of a 10% solution of phosphoric acid is shown in Fig. 8 (*D*). The acid-resistant white cover enamel was very resistant to attack. The other enamels showed widely scattered degrees of surface attack. The antimony cover and ground-coat enamels were quite resistant to the attack of the 10% acid; the blue zirconium cover and the sign blue cover enamels, an intermediate amount; and the other two surfaces, the white zirconium and white fluoride cover enamels, a high amount of attack, the fluoride enamel showing a greater rate than the white zirconium cover enamel.

(ix) *Effect of Fresh Solutions for Each Time Period:* In order to compare the repeated use of the same solution and a fresh solution for each time period, a few tests were run with 1% and 10% solutions. The results are summarized in Table III.

In Fig. 9 (*A*), the effects of the 1% solutions on the fluoride white cover enamel are compared. The solid lines represent the initial condition in which the same solution was used throughout the test run, while the broken lines show the effect of using a fresh sample of solution for each time period. Of particular importance is the sharp increase in the chemical attack when a fresh solution was used for each time interval. The increase due to the use of the fresh solutions, moreover, was proportional to the attack obtained when the same solution was used throughout a test run. When the fresh solutions were used for each time period, all four of the 1% solutions of the mineral acids attacked the fluoride enamel coating so rapidly and to such a pronounced extent that the enamel surfaces were broken through after the 20- or the 40-hour time periods.

The effects of the 1% solutions of the mineral acids on the antimony white cover enamel are compared in Figs. 9 (*B*) and 9 (*C*). In Fig. 9 (*B*), the effects of the 1% solutions of nitric and sulfuric acids, when the same solution was used throughout the test run, are shown as the solid lines; the broken lines indicate the chemical attack when a new solution was used for each time period.

In Fig. 9 (*C*), the effects of the 1% solutions of hydrochloric and phosphoric acids were plotted. The solutions of hydrochloric, nitric, and sulfuric acids showed the same general trend on the antimony white cover as observed on the fluoride enamels, only to a lesser degree; but the 1% solution of phosphoric acid showed exactly the same chemical effect when it was changed for each time interval as when it was used throughout a test run. Comparison of the effects of the 10% solutions showed that there is not so great an increase in the total attack when new solutions are used for each time period as with the 1% solutions.

These tests indicate that with the 1% solutions of hydrochloric, nitric, sulfuric, and phosphoric acids (on the fluoride enamel) when the same solution was used throughout a test run, the actual acid strength was depleted so that no further chemical action could take place; when a new solution was used in each time period, the fresh acid brought about increased solubility. The effect of the ions produced by the chemical attack on the enamel surfaces also tended to reduce further activity. With the 10% solutions, the effect of changing the solution for each time interval was not nearly so pronounced because the total decrease in the acid strength was much less than that of the 1% solutions.

(*B*) *Effect of Organic Acids:* The comparative chemical attack of 10% solutions of selected organic acids on the various porcelain enamel surfaces is shown in Figs. 10 to 15.

Figure 10 shows the effect of 10% acetic acid on the

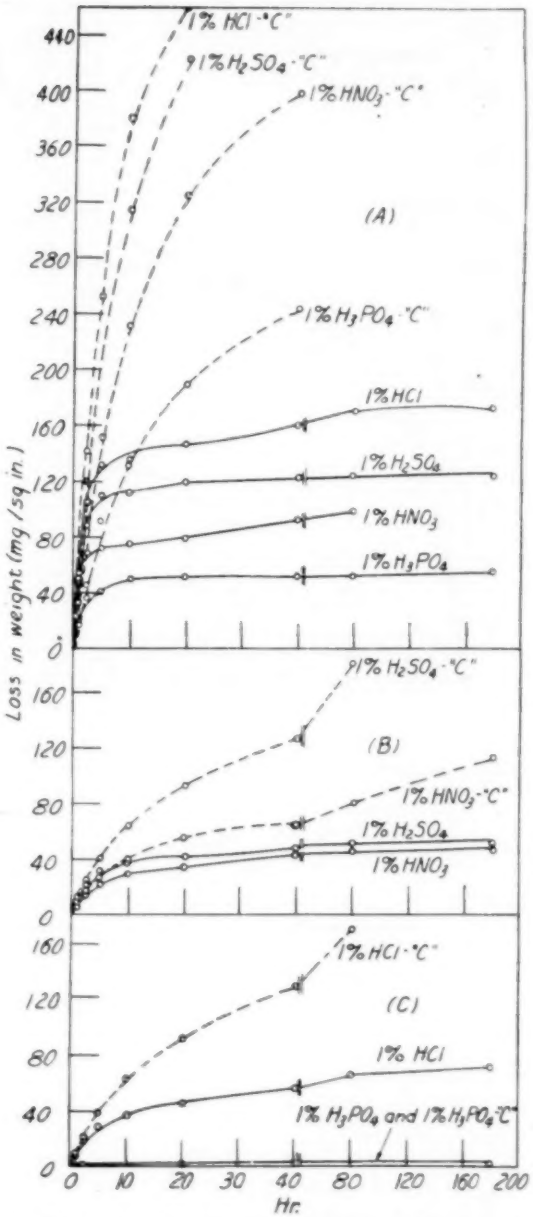


FIG. 9.—Comparison on cover enamels of new solutions and the same 1% solutions of (*A*) mineral acids on fluoride white, (*B*) $H_2SO_4$ and $HNO_3$ on antimony white, and (*C*) HCl and $H_3PO_4$ on antimony white.

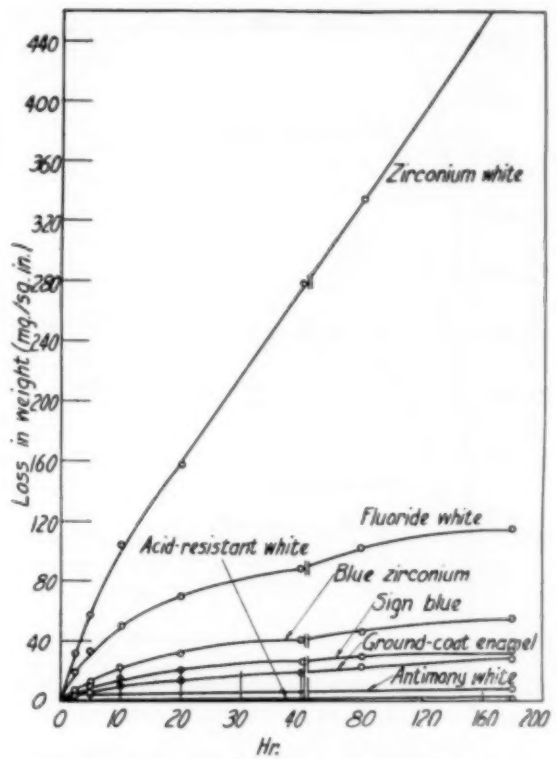


FIG. 10.—Effect of 10% acetic acid on various enamel surfaces at room temperature (all cover enamels except one ground coat).

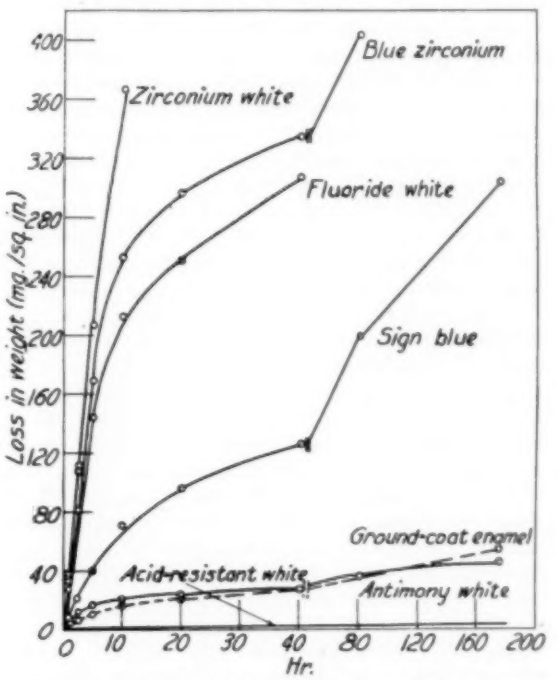


FIG. 11.—Effect of 10% citric acid on various enamel surfaces at room temperature (all cover enamels except one ground coat).

various enamel surfaces. In general, the surfaces are quite resistant to the attack of acetic acid as none was broken through after a total of 180 hours. The acid-resistant white and antimony cover enamels were only slightly attacked. The ground-coat, sign blue cover, and blue zirconium cover enamels were attacked to an increasing degree. The fluoride white cover enamel exhibited a moderate amount of attack, while the white zirconium cover enamel showed an appreciable degree of chemical attack.

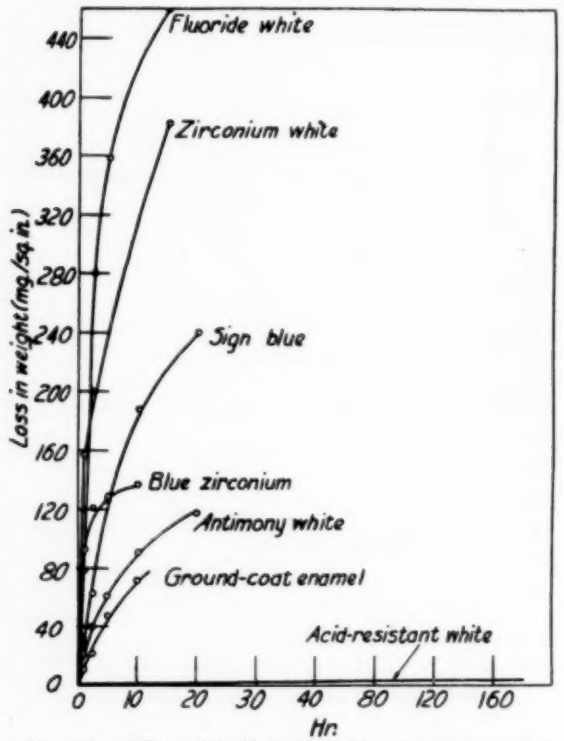


FIG. 12.—Effect of 10% oxalic acid on various enamel surfaces at room temperature (all cover enamels except one ground coat).

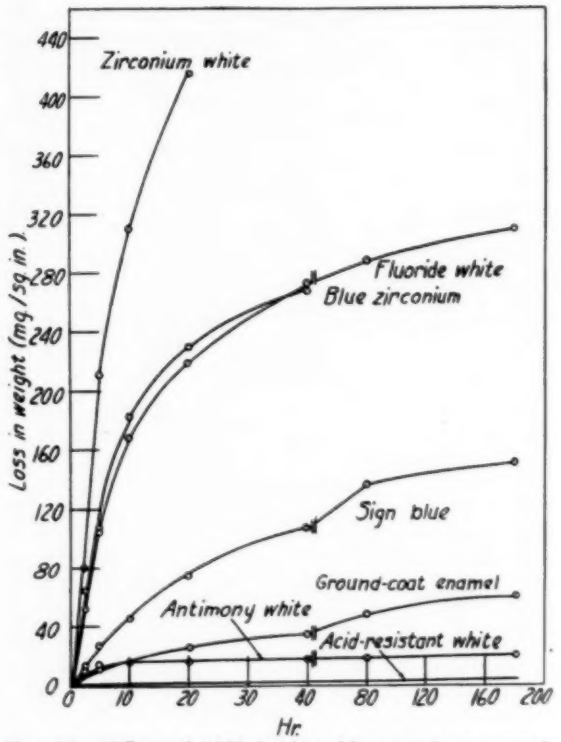


FIG. 13.—Effect of 10% lactic acid on various enamel surfaces at room temperature (all cover enamels except one ground coat).

The effect of a 10% solution of citric acid on the selected group of enamel surfaces is shown in Fig. 11. A wide variation in the rate and total amount of chemical attack is exhibited. The acid-resistant white cover enamel showed practically no chemical attack; the ground-coat and the antimony white cover enamels showed a low loss in weight; while the sign blue cover enamel exhibited a moderate loss. The fluoride white cover and blue zirconium cover enamels showed a high loss in weight, the surface being broken through in 40 and 80 hours, respectively. The 10% citric acid attacked the white zirconium cover enamel to a high degree, breaking through the surface in 10 hours.

Figure 12 shows the effect of a 10% solution of oxalic acid on the enamel surfaces. In general, the acid-resistant white cover enamel is very resistant to the attack of oxalic acid, while the other enamel surfaces are attacked to a considerable degree. Except for the acid-resistant white, the ground-coat enamel showed the lowest rate of weight loss, but the surface was broken in 10 hours. The antimony white cover enamel showed a greater rate of loss than the ground coat, but the surface was not broken until after 20 hours. The sign blue cover enamel showed the next higher rate of acid attack and also a high amount of total attack, the surface being broken through after 20 hours. The blue zirconium cover enamel showed a greater initial rate of loss than the sign blue cover enamel, but the total loss before the surface was broken was considerably less. The zirconium and fluoride

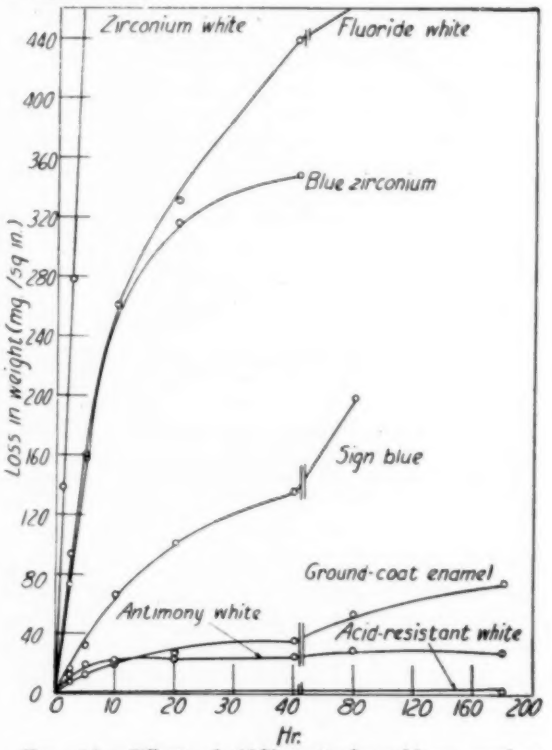


FIG. 14.—Effect of 10% tartaric acid on various enamel surfaces at room temperature (all cover enamels except one ground coat).

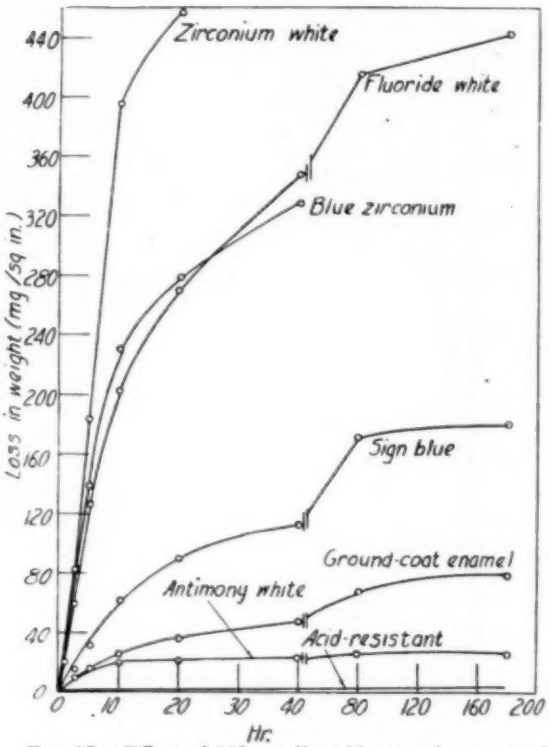


FIG. 15.—Effect of 10% malic acid on various enamel surfaces at room temperature (all cover enamels except one ground coat).

white cover enamels showed a high loss in weight from the action of the oxalic acid.

Figure 13 shows the general effect of a 10% solution of lactic acid on the various enamel surfaces. A wide variation in the rate and total amount of chemical attack was exhibited by the different enamel surfaces. The acid-resistant white cover enamel was very resistant to the lactic acid. The antimony white cover and the ground-coat enamels showed about the same relatively low loss in weight for the first 10 hours; thereafter, the antimony white enamel showed practically no additional loss while that of the ground coat increased until at 180 hours the total attack was about three times as much as for the antimony cover enamel. The sign blue cover enamel showed a moderate rate of attack with the total loss in weight double that obtained for the ground coat at the 180-hour period. The fluoride white cover and blue zirconium cover enamels showed a high loss in weight and the zirconium white cover enamel, an even greater loss.

In Fig. 14, the effect of a 10% solution of tartaric acid on the various enamel surfaces is plotted. The different enamels exhibited wide variations in their comparative resistances to the acid. The acid-resistant white cover enamel showed practically no attack; the antimony white cover, a slight attack; and the ground-coat, an increasing amount. The sign blue cover enamel showed a moderate amount of loss; the blue zirconium cover and fluoride white cover enamels, a high amount of chemical attack; while the white zirconium cover

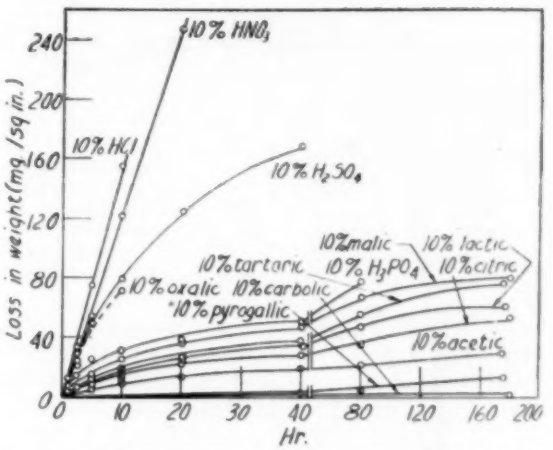


FIG. 16.—Chemical durability of ground-coat enamel at room temperature.

enamel showed the greatest attack of all the surfaces.

Figure 15 shows the effect of 10% malic acid on the various enamel surfaces. A wide variation in the rate and total amount of attack is exhibited. The acid-resistant white enamel showed almost negligible attack; the antimony white cover enamel, a small amount of chemical attack; the ground-coat, an increased amount; and the sign blue cover enamel, a moderate amount. The fluoride white cover and blue zirconium cover enamels showed a rapid loss in weight, while the white zirconium cover showed the greatest loss of any of the surfaces.

The other two organic acid solutions, the 10% pyrogallic and 10% carbolic acids, in general, showed little chemical attack on the different enamel surfaces so that it was difficult to indicate the results graphically. The carbolic acid showed less attack than 1 mg. per sq. in. of surface after 180 hours for all of the selected enamel finishes. The pyrogallic acid, however, showed slightly greater attack, a particularly high amount being obtained on the white zirconium and blue zirconium cover enamels.

In summarizing the general effect of the selected organic acids on the various enamel surfaces at room temperature, it is to be noted that (1) a 10% solution of oxalic acid showed almost as much chemical attack as a 10% solution of the inorganic acids; (2) 10% solutions of citric, tartaric, lactic, and malic acids, respectively, showed about the same general type and amount of attack on the different surfaces; (3) a 10% solution of acetic acid was relatively weak when compared with the organic acids; and (4) the 10% solutions of pyrogallic and carbolic acids showed relatively low chemical attack on the different porcelain enamel surfaces.

In order to summarize and compare the relative degree and rate of attack of the different organic and inorganic acids on the various enamel surfaces, the groups of curves plotted in Figs. 16 to 20 are presented.

In Fig. 16, the effects of 10% solutions of the organic and inorganic acids on the ground coat are given. The 10% solutions of hydrochloric and nitric acids showed the greatest degree of attack, while the 10% solutions

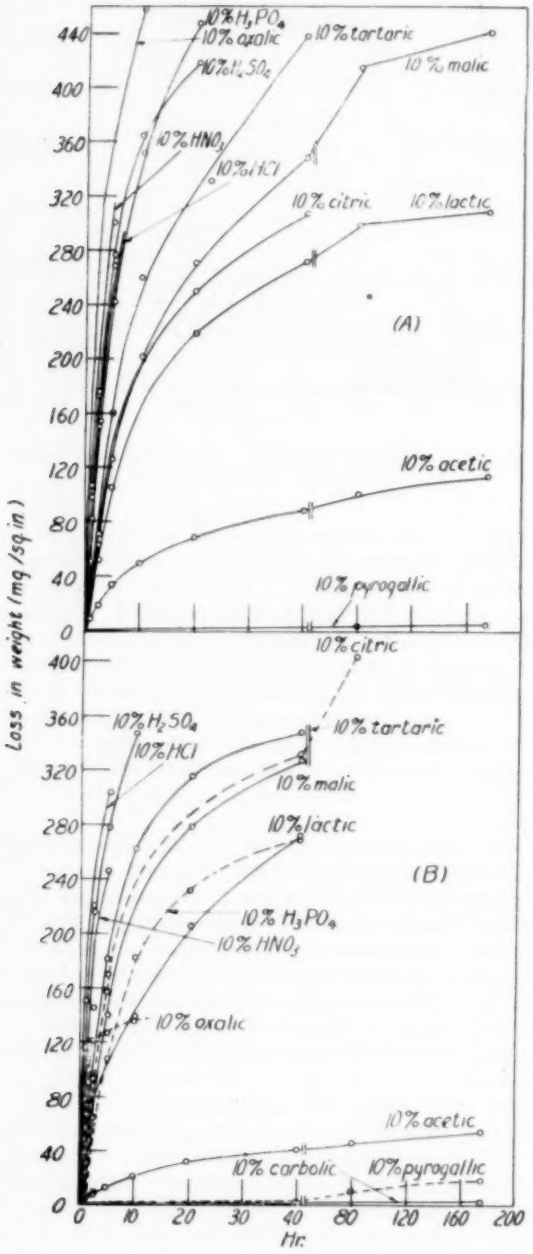


FIG. 17.—Chemical durability of two cover enamels at room temperature: (*A*) sign blue and (*B*) white antimony.

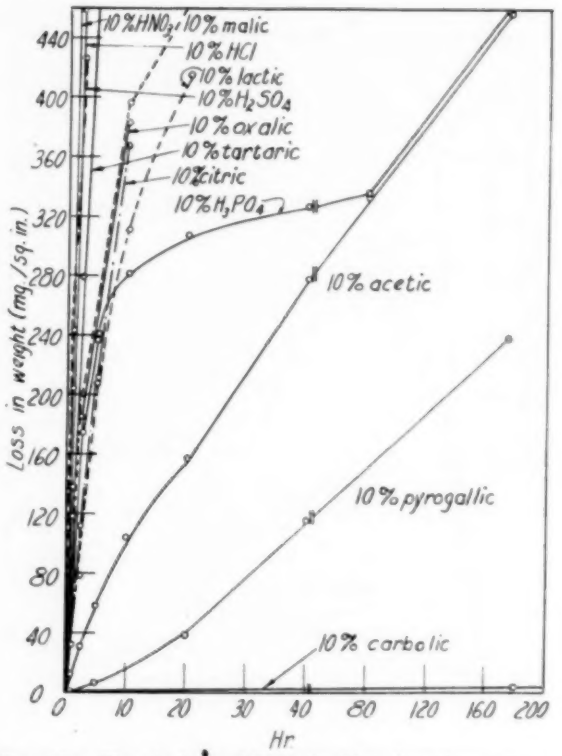


FIG. 18.—Chemical durability of white zirconium cover enamel at room temperature.

of sulfuric and oxalic acids showed about the same rate, although the oxalic acid broke through the surface after 10 hours. The 10% solution of phosphoric acid showed slightly greater attack than the remainder of the organic acids. Of these acids, other than the oxalic, the general contour of the curves was about the same, with the degree of attack decreasing in the order of malic, tartaric, lactic, and citric acids. The 10% solution of acetic acid showed lower attack than the preceding group of acids, the 10% solution of pyrogallic acid showed still less attack, and the 10% solution of carbolic acid showed practically no attack.

The effects of the 10% solutions of the organic and inorganic acids on the sign blue cover enamel are shown in Fig. 17 (*A*). The 10% solutions of hydrochloric and nitric acids showed the greatest attack, while the oxalic acid showed slightly greater attack than the sulfuric and phosphoric acids. The curves of the four organic acids, citric, tartaric, malic, and lactic, were grouped in the intermediate range. The acetic acid showed weak attack; the pyrogallic, a very slight amount; and the carbolic acid, practically none.

In Fig. 17 (*B*), the effects of the 10% solutions of the organic and inorganic acids on the antimony white cover enamel are given. The general order of decreasing total attack as well as the total rate of attack is as follows: hydrochloric, nitric, sulfuric, and oxalic acids. The phosphoric acid, which had less initial attack than the intermediate group of organic acids, showed greater total attack. The intermediate group of organic acids, citric, tartaric, malic, and lactic, showed slightly greater attack than the acetic and pyrogallic acids, while the carbolic acid showed less than 1 mg. total attack in 175 hours.

In Fig. 18, the effects of the 10% solutions of the organic and inorganic acids on the zirconium white cover enamel are shown. This cover enamel is particularly subject to attack by most of the inorganic and organic acids. The 10% solutions of nitric, hydrochloric, and sulfuric acids showed a slightly greater degree of

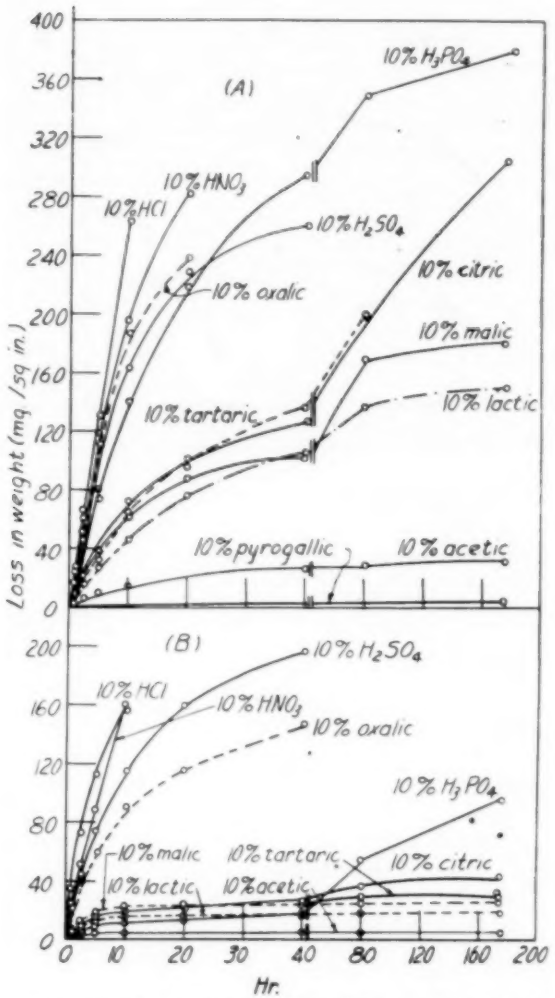


FIG. 19.—Chemical durability of two cover enamels at room temperature: (*A*) white fluoride and (*B*) blue zirconium.

attack than the tartaric acid. Another group of acids, bunched together and showing a high degree of total attack, were malic, oxalic, citric, and lactic acids, in order of slightly decreasing attack. The phosphoric acid showed a high initial rate of chemical attack, decreasing somewhat after 10 hours. The 10% solution of acetic acid showed pronounced attack; the 10% solution of pyrogallic acid showed a manyfold increase in attack on the zirconium white cover enamel over that of the other surfaces. The 10% solution of carbolic acid was the only test solution that showed no appreciable attack on the zirconium white cover enamel.

In Fig. 19 (*A*), where the effects of 10% solutions of the organic and inorganic acids on the white fluoride enamel surfaces are summarized, the different acids are shown to vary widely in their degree of chemical attack. The 10% oxalic acid showed the greatest attack, while the 10% solutions of nitric, sulfuric, hydrochloric, and phosphoric acids showed slightly lower attack. The attack of the four organic acids, tartaric, malic, citric,

TABLE IV

CHEMICAL DURABILITY OF ENAMEL SURFACES IN CONTACT WITH SODIUM HYDROXIDE AT ROOM TEMPERATURE

| | 10% sodium hydroxide (loss in weight (gm./sq. in.)) | |
|---|---|---|
| Cover enamel surface | 100 hr. | 1000 hr. |
| Fluoride white | 0.00075 | 0.00416 |
| Antimony white | .00043 | .00268 |
| Zirconium white | .00142 | .0165 |
| Acid-resistant white | .00013 | .00248 |
| Sign blue | .00060 | .00476 |
| Zirconium blue | .00040 | .00308 |

and lactic, varied over a considerable range, decreasing in the order listed. The 10% solution of acetic acid showed comparatively low attack; the pyrogallic acid, a slight amount; while the carbolic acid showed a loss in weight of less than 1 mg. per sq. in.

In Fig. 19 (*B*), the effect of the 10% solutions of the organic and inorganic acids on the blue zirconium cover enamel is given. In general, this enamel surface is attacked to a considerable degree by most of the organic and inorganic acids. The hydrochloric, sulfuric, and nitric acids showed rapid attack and the tartaric, citric, and malic acids, a slightly lower rate. The attack of the lactic and phosphoric acids was about the same but still less rapid. The initial rate of attack of the oxalic acid was slightly less than the strong mineral acids but the total attack was much lower. The acetic acid showed relatively low attack; the pyrogallic acid, a slight amount; and the carbolic acid, practically none.

(*C*) *Effect of Alkalis:* In determining the resistance of porcelain enamel surfaces to alkalis at room temperature, a solution of sodium hydroxide seemed to be the most representative. The results of allowing a 10% solution to remain in contact with the selected enamel surfaces for periods of 100 hours and 1000 hours are shown in Table IV. The zirconium white cover enamel is the only surface to show a loss in weight greater than 1 mg. per sq. in. after standing for 100 hours. In the 1000-hour period, there was an appreciable loss in weight by the same enamel, increasing approximately tenfold over the 100-hour period. The remainder of the enamel surfaces showed about the same degree of attack in 1000 hours, all ranging from 2 to 5 mg. per sq. in.

(*D*) *Effect of Various Salts:* In general, the various salt solutions showed, essentially, no measurable loss in weight when standing in contact with the different enamel surfaces at room temperature.

## (2) Chemical Durability at Boiling Temperatures

The chemical solutions, which showed very low total attack on the various enamel surfaces at room temperature, were investigated in further detail under boiling conditions. The solutions were placed in weighed test containers, a long-tube reflux condenser was clamped in place, and the various chemical solutions in the test cups were boiled vigorously on an electric hotplate for time intervals of 10, 25, 50, and 100 hours.

(*A*) *Effect of Inorganic Acids:* In studying the effect of the different inorganic acids on the various

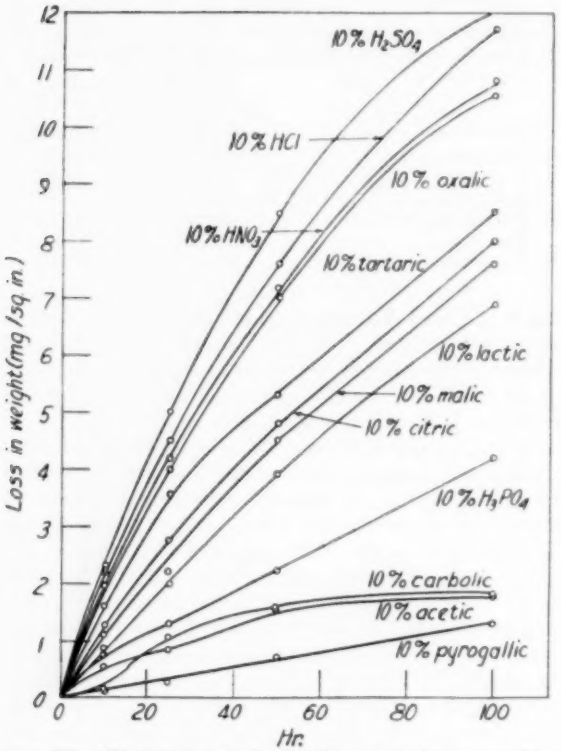


FIG. 20.—Chemical attack of boiling solutions on acid-resistant white enamel surfaces.

enamel surfaces at room temperature, most of the surfaces were attacked to a considerable degree. Two enamel surfaces, the acid-resistant white cover and chemical acidproof cover, were attacked slightly at room temperature. Consequently, the effect of the different inorganic acids on these surfaces was investigated at boiling temperatures.

In Fig. 20, plotted curves show the effects of the chemical attack of boiling 10% solutions of inorganic acids as well as selected organic acids on the acid-resistant surfaces. The organic acids will be analyzed in detail in section IV (2, *B*), but the curves were plotted on the same figure so that they could be readily compared.

In comparing the effects of the inorganic acids, the 10% solution of sulfuric acid showed the greatest attack, while the solutions of hydrochloric and nitric acids showed slightly less attack. The boiling 10% solution of phosphoric acid caused less than half the total attack of the other inorganic acids.

The effects of the boiling inorganic acid solutions on the chemical acidproof cover enamel are shown in Fig. 21 (*A*). The total chemical attack on the acidproof enamel is very low, approximately one third that shown on the acid-resistant white cover. Figure 21 (*A*) also shows that the 10% solution of hydrochloric acid resulted in greater attack on the chemical acidproof enamel than either the sulfuric or nitric acids, but the latter acids showed slightly greater attack than the phosphoric acid. With all four of the inorganic acids, the amount of attack was very low.

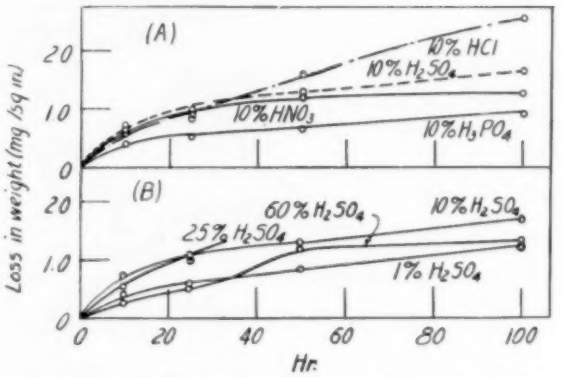


FIG. 21.—Chemical attack on chemical acidproof enamels: (*A*) effect of boiling inorganic acids and (*B*) effect of different concentrations of boiling $H_2SO_4$.

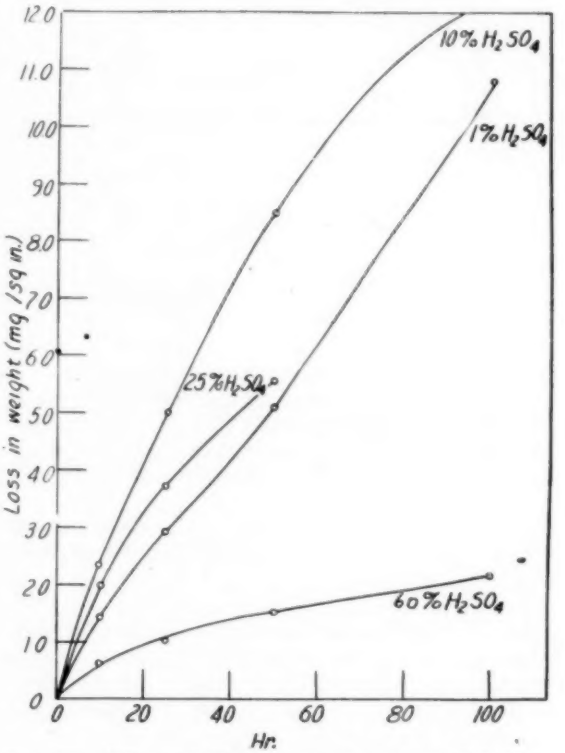


FIG. 22.—Effect of different concentrations of boiling $H_2SO_4$ on acid-resistant white cover enamel.

In order to study the comparative effect of different concentrations of an inorganic acid at boiling temperatures, 1%, 10%, 25%, and 60% solutions of sulfuric acid were selected.

Figure 21 (*B*) shows the loss in weight when the chemical acidproof enamel is subjected to the attack of the different concentrations of sulfuric acid under boiling conditions. The total loss in weight of the 1%, 10%, and 60% solutions was very low and close to the same value; however, with the 25% solution, the rate of attack for the first 25 hours was approximately the same as that of the 10% solution, but the acid broke

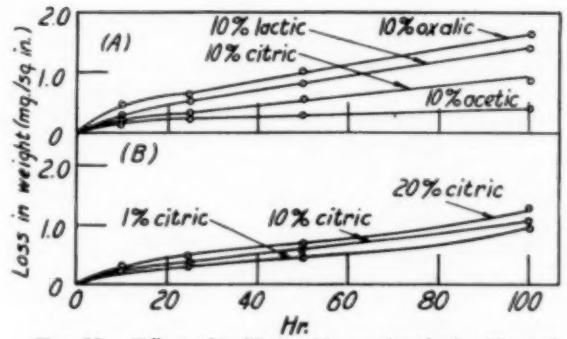


FIG. 23.—Effect of boiling acids on chemical acidproof enamel: (*A*) effect of organic acids and (*B*) effect of different concentrations of citric acid.

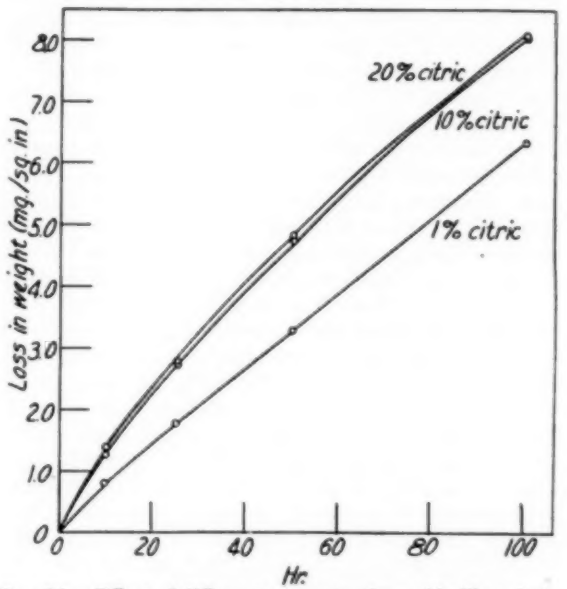


FIG. 24.—Effect of different concentrations of boiling citric acid on acid-resistant white cover enamel.

through the enamel surface in a small area after the 25-hour period. Although, in this case, the total loss in weight was of the order of 1 mg. per sq. in., the enamel surface was fractured in a localized spot.

In Fig. 22, the effects of the different concentrations of sulfuric acid under boiling conditions on the acid-resistant white cover enamel are presented. The 10% solution showed the greatest rate and highest total attack. Although the actual rate of the 25% solution of sulfuric acid was less than that of the 10% solution, the 25% solution broke through the surface after 50 hours; the 1% solution showed less attack than the 10% solution; and the 60% solution showed very low but slightly increasing attack over 100 hours.

(*B*) *Effect of Organic Acids:* In general, the same enamel surfaces that showed appreciable attack by the inorganic acids at room temperature were attacked to a considerable degree by most of the organic acids at boiling temperatures.

Figure 20, previously mentioned, shows the effects of the boiling organic and inorganic acid solutions on

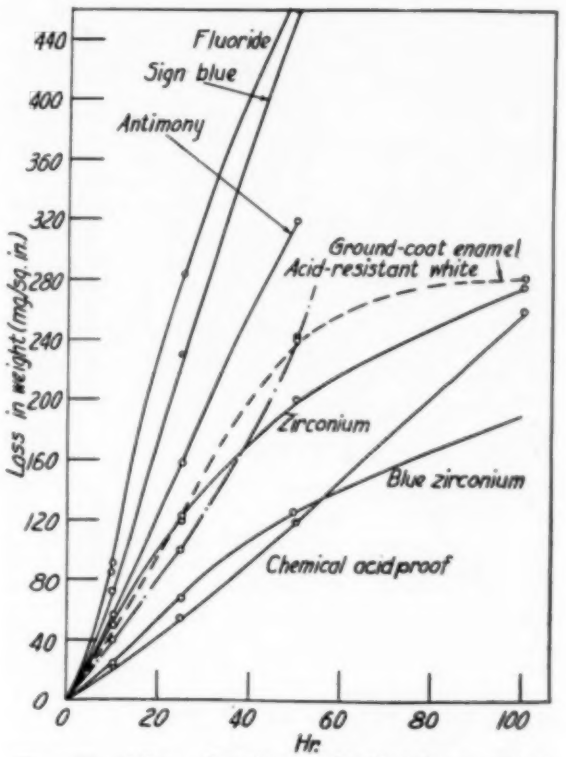


FIG. 25.—Effect of boiling 10% NaOH on various enamel surfaces (all cover enamels except one ground coat and a chemical acidproof).

the acid-resistant white cover enamel. The 10% solution of oxalic acid showed the greatest attack of any of the organic acids, being slightly less than that of the nitric acid. The four organic acids, tartaric, citric, malic, and lactic, attacked the acid-resistant white cover enamel to a comparable degree, the total amount of acid attack decreasing in the order named. The 10% acetic and 10% carbolic acids showed about the same relative low amount of attack, while the 10% solution of pyrogallic acid showed still less.

In Fig. 23 (*A*), the chemical effect of representative organic acids on the acidproof cover enamel is given. The total attack of even the oxalic acid was quite low, and the 10% solution of lactic acid showed slightly less attack. The curve showing the effect of the 10% solution of tartaric acid was not plotted as it was almost identical with that of the 10% lactic acid. The 10% solution of citric acid showed still less attack than the tartaric and lactic acids. The curve for the 10% solution of malic acid was not plotted as it followed very closely that of the citric acid. The 10% solution of acetic acid exhibited about half as much total attack as the citric and malic acids. Because the carbolic and the pyrogallic acids showed about the same or slightly greater attack than the acetic acid, they were not plotted. The total loss in weight of the acidproof enamel, when subjected to the action of boiling organic acids, was less than 2 mg. per sq. in. in 100 hours.

In Fig. 23 (*B*), the effects of 1%, 10%, and 20%

TABLE V

EFFECT OF SELECTED SALT SOLUTIONS AT BOILING TEMPERATURES ON ENAMEL SURFACES

Loss in weight (gm. per sq. in.); time (100 hours)

| 10% chemical solution | Ground-coat enamel | Cover enamels | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Fluoride | Antimony | Zirconium | Acid-resistant | Acidproof | Sign blue | Blue zirconium |
| NaCl | 0.00076 | 0.00045 | 0.00019 | | 0.0008 | 0.00054 | 0.00009 | 0.00006 |
| $Na_2CO_3$ | .01213 | .00378 | .00272 | 0.00241 | .00990 | .01442 | .01358 | .00309 |
| $Na_2B_4O_7$ | .00269 | .00264 | .00173 | .00266 | .00252 | .00306 | .00191 | .00228 |
| $NaHCO_3$ | .00403 | .00347 | .00079 | .00264 | .00556 | .01900 | .13380 | .00136 |
| $MgSO_4$ | .00131 | .00103 | .00080 | .00123 | .00069 | .00276 | .00029 | .00059 |
| $Na_2SO_4$ | .00139 | .00072 | .00059 | .00030 | .00035 | .00180 | .00029 | .00046 |
| $Na_2SO_3$ | .00266 | .00089 | .00036 | .00103 | .00707 | .00126 | .00045 | .00033 |
| $Na_3PO_4$ | .06945 | .01920 | .02880 | .01721 | .03190 | .06770 | .18150 | .01030 |
| $Na_2HPO_4$ | .00307 | .00151 | .00132 | .00171 | .00191 | .00743 | .00117 | .00096 |
| $NaNO_3$ | .00043 | .00046 | .00030 | .00015 | .00024 | .00042 | .00192 | .00046 |
| $ZnCl_2$ | .00250 | .00750 | .00330 | .01620 | .00102 | | .00657 | .00392 |
| $AlCl_3$ | .03765 | .12310 | .02060 | .17400 | .00114 | .00053 | * | .05370 |

* Gain in weight due to deposition of adherent residue.

solutions of citric acid at boiling temperatures on the acidproof enamel are given. The degree of attack is shown to increase only slightly from the 1% through the 10 to 20% citric acid solutions, and the total attack is very low, approximately 1 mg. per sq. in.

In the series of three curves shown in Fig. 24, the effects of the 1%, 10%, and 20% solutions of citric acid at boiling temperatures on the acid-resistant white cover enamel are given. The degree of attack of the 10% and 20% solutions was similar while that of the 1% acid was uniformly lower.

(*C*) *Effect of Alkalis:* As was stated in previous results, the chemical attack of a 10% solution of sodium hydroxide on the various enamel surfaces at room temperature was relatively low. Therefore, the effect of a boiling 10% solution on the various enamel surfaces was determined. The loss in weight, expressed as grams per square inch at time intervals of 10, 25, 50, and 100 hours for each of the different surfaces, is plotted in Fig. 25. The white fluoride cover enamel was attacked the most rapidly of all the surfaces, with the sign blue cover enamel showing almost as much total attack by the boiling alkaline solution. The fluoride, sign blue antimony, and the acid-resistant cover enamels were attacked so rapidly that the under surfaces were exposed after 50 hours. The ground coat and the zirconium white cover coat showed about the same rate of loss in the first 50 hours as the antimony cover and acid-resistant white enamels, but the curves began to flatten after 50 hours and the surface was not broken in the 100-hour period. The chemical acidproof and blue zirconium enamels were the most resistant to the attack of the boiling solution, the acidproof enamel showing a higher total loss in weight than the blue zirconium. None of the enamel surfaces was resistant to the attack of the boiling 10% solution of sodium hydroxide.

(*D*) *Effect of Selected Salts:* Since the comparative attack at room temperature of the selected salt solutions on the various enamel surfaces was very low, the resistances of the enamel surfaces to the attack of the boiling salt solutions were determined. The data in Table V summarize the action of the boiling salt solutions for 100 hours. All eight of the enamel surfaces were resistant to the action of a 10% sodium chloride solution. The acidproof, acid-resistant, sign blue, and ground-coat enamels were attacked to an appreciable extent by the 10% sodium carbonate solution, while the other four enamel surfaces were only slightly affected. The 10% solution of sodium borate showed equally low attack on all the enamels. The 10% solution of sodium bicarbonate showed erratic results, some surfaces being attacked appreciably while others were practically unaffected. The 10% solutions of magnesium sulfate, sodium sulfate, sodium sulfite, and sodium nitrate showed relatively low attack. The solution of trisodium phosphate showed decided attack on all of the enamels. The action of the disodium acid phosphate solution was considerably less than that of trisodium phosphate. The 10% solution of zinc chloride showed the greatest attack on the zirconium and fluoride white cover and on the sign blue cover enamels. The 10% solution of aluminum chloride showed appreciable attack on practically every surface except the acid-resistant and acidproof enamels. When the 10% solution of aluminum chloride was in contact with the sign blue cover enamel, the container showed gain in weight due to the deposition of an adherent residue.

In general, as shown by the limited number of salt solutions investigated, the solutions, which, on hydrolysis, were predominantly acidic, attacked the non-acid-resistant surfaces, while only slight attack occurred on the acid-resistant surfaces. Further, the salt solutions that gave a basic reaction showed considerable attack on the acid-resistant surfaces and variable attack on the other enamels. Of the salt solutions investigated, aluminum chloride showed appreciable attack on all enamels except the acid-resistant surfaces; and trisodium phosphate, showed marked attack on all of the enamel surfaces.

### (3) Microscopic Study and Selected Photomicrographs of Representative Surfaces

In order to study the nature and the mechanism of the chemical attack, the various enamel surfaces were examined under the microscope, and photomicrographs were made of the representative surfaces. In general, it was found that the action of (*a*) a 10% solution of sulfuric acid for one hour, (*b*) a 10% solution of citric acid for one hour, and (*c*) a 10% boiling solution of

sodium hydroxide for 10 hours gave characteristic patterns of attack on the different enamel surfaces.

(*A*) *Ground-Coat Enamel:* When the ground-coat enamel surfaces were examined under the microscope, the type of pattern of the citric and sulfuric acids was similar. Figure 26 (*A*) shows a ground-coat enamel surface after exposure to the attack of a 10% solution of sulfuric acid for one hour. The photomicrograph shows that the bubble structure of the ground-coat surface is appreciably altered, a fine interlocking network of surface cracking is present, and appreciable etching has taken place (shown by the lighter areas).

The pattern of attack after exposing the ground-coat surface to the boiling 10% solution of sodium hydroxide for 10 hours is quite different from that shown by the acid attack. A much larger pattern of attack is apparent, and the degree of surface solution appears to be much greater.

(*B*) *Fluoride White Cover Enamel:* The nature and type of acid action on the fluoride enamel surfaces, as observed under the microscope, show a "mud-cake" pattern of attack. Figure 26 (*B*) shows the effect of a 10% solution of sulfuric acid for one hour; with the 10% solution of citric acid, the size of the pattern of attack is much smaller.

The pattern of attack after exposing the fluoride enamel to the boiling 10% sodium hydroxide solution for 10 hours is considerably different from that shown by the acid attack. With the boiling alkaline solution, there is no specific pattern, but the surface appears very porous, which would indicate that a considerable amount of solution had taken place.

(*C*) *Antimony White Cover Enamel:* Figure 26 (*C*) shows the type of attack or pattern obtained from the action of a 10% solution of sulfuric acid on the antimony enamel for one hour. The size of the pattern is much smaller than that of the fluoride enamel, and the space between the pattern agglomerates is considerably decreased. The size of the pattern resulting from the attack of citric acid is much smaller than that shown by the sulfuric acid.

The pattern of attack on the antimony enamel surface after exposure to the boiling 10% sodium hydroxide solution is not at all comparable with that of the acid attack. After the action of the boiling alkaline solution, the surface appears very porous and pockmarked, indicating a considerable amount of solution to have taken place.

(*D*) *Zirconium White Cover Enamel:* When the zirconium white cover enamel is examined under the microscope, an entirely different type of attack is observed than that shown on the fluoride or antimony white enamel surfaces. After the action of the 10% solutions of sulfuric or citric acids, the surface appears porous and pitted, showing evidence of considerable solution. In addition, the zirconium-enamel surface remaining after acid attack is hard and not readily scratched by a sharp-pointed instrument, in contrast with the fluoride and antimony enamels, in which particles on the surface are rather powdery and easily dislodged.

Figure 27 (*A*) shows the zirconium surface after

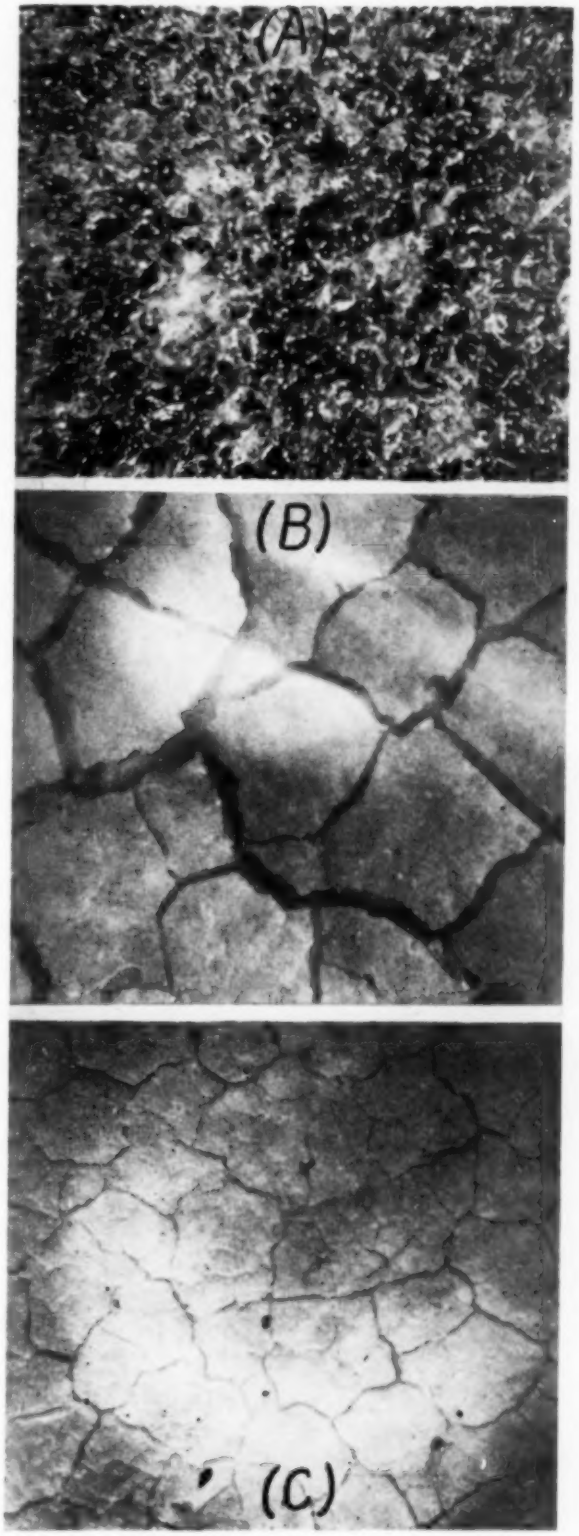


FIG. 26.—Photomicrographs of enamel surfaces after attack of 10% sulfuric acid solution for one hour (×60): (*A*) ground coat, (*B*) fluoride white cover, and (*C*) antimony white cover.

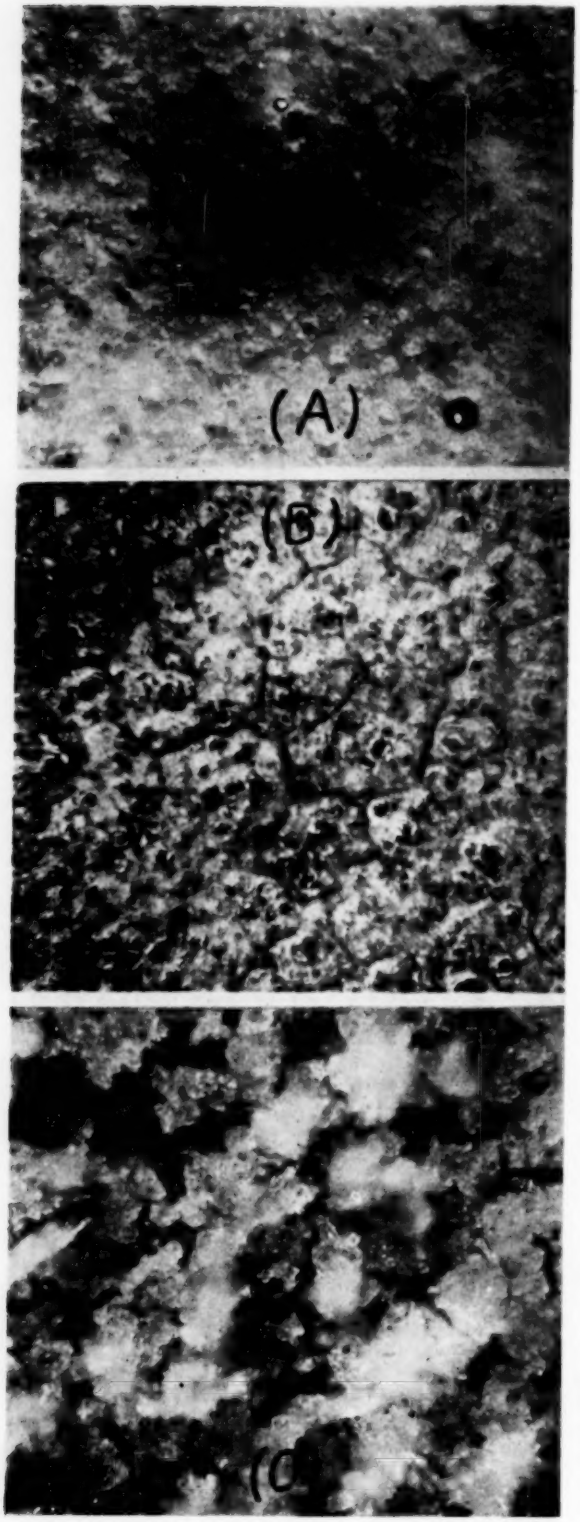


FIG. 27.—Photomicrographs of enamel surfaces after attack of 10% sulfuric acid for one hour (×60): (*A*) zirconium white cover, (*B*) sign blue cover, and (*C*) blue zirconium cover.

exposure to a 10% solution of sulfuric acid for one hour; the surface appears uneven, rough, and pitted. The surface attack is similar for the 10% solution of citric acid although not quite so pronounced.

The nature of the surface of the zirconium enamel after being subjected to a boiling sodium hydroxide solution for 10 hours looks similar to the surface after the acid attack; it is rough, pitted, and shows considerable evidence of solution.

(*E*) *Sign Blue Cover Enamel:* A photomicrograph of the sign blue cover enamel surface after being exposed to the attack of a 10% solution of sulfuric acid is shown in Fig. 27 (*B*).

The acid attacks the surface, leaching out the coloring components, and leaves a transparent-to-translucent etched surface; the surface, furthermore, shows a definite pattern. The surface exposed to the attack of the citric acid is similar except that the penetration is not so deep and the pattern is much smaller.

When the sign blue enamel surface, after contact with boiling sodium hydroxide solution, is examined under the microscope, the surface is rough, uneven, and deeply etched, showing the action of solution attack. Further, no definite pattern is observed, and the coloring agents in the enamel surface are not selectively leached out as shown by the acid attack.

(*F*) *Blue Zirconium Cover Enamel:* Figure 27 (*C*) shows the blue zirconium enamel after being attacked by the 10% solution of sulfuric acid for one hour. The photomicrograph shows transparent powdery particles on the surface along with a rosette crystalline material that was not identified. Underneath the loosely adherent particles, the surface was quite hard, dense, and apparently unattacked. The 10% citric acid showed a comparatively small amount of attack when the surface was observed under the microscope.

With the boiling alkaline solution on the blue zirconium enamel, small, powdery opaque particles are left on the hard, dense enamel surface.

(*G*) *Acid-Resistant and Acidproof Enamels:* The acid-resistant and acidproof enamel surfaces, after exposure to the boiling acid solutions, were examined under the microscope. At first, only an iridescent film appeared on the surface; after prolonged attack, the acid seemed to penetrate below the surface in certain localized areas, which, on drying, due to the presence of an air space below the surface, appeared as a lighter opaque area. With further action, the enamel surface over this lighter area was forced off, thus exposing the underneath surface to additional attack. In time, the action of the acid exposed the metal surface.

When the acid-resistant and acidproof enamel surfaces were examined under the microscope after exposure to the 10% boiling sodium hydroxide solution for 10 hours, a hard, but porous, etched surface was observed, which indicated appreciable solution of the enamel surface.

## V. Analyses of Results

As an aid in analyzing the results of the attack of the various chemical solutions on the different enamel surfaces, the mechanism and nature of the chemical

action may be considered from the viewpoint of the effect of (1) acids on the non-acid-resistant enamel surfaces, (2) acids on acid-resistant enamel surfaces, (3) alkalis on porcelain enamels, and (4) selected salt solutions on various enamel surfaces.

### (1) Effect of Acids on Non-Acid-Resistant Surfaces

In general, when an organic or inorganic acid is brought in contact with non-acid-resistant surfaces, the gloss is progressively destroyed, a decided etch is imparted to the surface, and the enamel coating is destroyed until only a fine powdery dust remains.

In explaining the action of the various organic and inorganic acid solutions on the different porcelain enamel surfaces, it might be postulated that, since silica is the predominant constituent in porcelain enamels, it would form a relatively loose random structural arrangement in which the other constituents, such as B, Al, Na, K, Ca, and others, would either replace silicon or be distributed at random in the holes in the structural network. When the porcelain enamel coating is subjected to acid attack, either (*a*) the more soluble materials, such as Na, K, B, and others, would be progressively leached out of the structural network, leaving a silica-enriched layer, or (*b*) the entire structure would be systematically and uniformly attacked and decomposed. In (*a*), where a silica-enriched layer would be left in contact with the acid solution, the silica would remain as a hydrated or gel-like material; the silica gel, on being dried, would shrink and pull apart, thus causing the sharp, jagged corners as observed in Fig. 26 and Fig. 27 (*B*). The four decidedly different non-acid-resisting enamels, the ground coat, fluoride cover, antimony cover, and sign blue cover enamels, show this characteristic. Further, the size of the pattern is dependent on the actual amount of the acid attack, which in turn is dependent on (i) enamel composition, (ii) the concentration and kind of acid, and (iii) the time period during which the acid is in contact with the enamel surface. The other two non-acid-resistant surfaces, the zirconium white cover and blue zirconium enamels, appear to be attacked as in supposition (*b*), in which the structure is systematically decomposed and the silica is completely removed rather than left as a layer of silica gel.

Secondary factors, such as the presence of crystallites, insoluble particles, or substances actually dissolved in the glassy phase, may influence the rapidity of chemical attack to a marked degree.

### (2) Effect of Acid on Acid-Resistant Enamel Surfaces

When an inorganic or organic acid is brought in contact with the acid-resistant surface, a slight loss in specular reflection or an iridescence may be imparted to the surface. With additional attack, the acid solution may penetrate the surface at some inhomogeneity, which then appears as a lighter opaque area; with further attack, the metal surface below is exposed.

In explaining the action of acid on these highly acid-resistant surfaces, the silica might be considered to form a dense close-packed structural arrangement in which the other elements are distributed in the holes in the network. When exposed to acid, the silica structure is not disturbed, but certain elements in the interstices of the network may be leached out causing the iridescence.

### (3) Effect of Alkalis on Porcelain Enamels

Alkaline solutions showed only slight attack on the porcelain enamel surfaces at room temperature. At boiling temperatures, the alkaline solutions showed rather rapid attack on all enamel surfaces. The enamel coating is progressively dissolved by the boiling alkaline solution, which leaves the surface porous and etched. The alkaline solution appears to attack and destroy the silica structure by dissolving the silica along with the other components in the enamel surface.

### (4) Effect of Salt Solutions on Porcelain Enamels

In analyzing the effect of the salt solutions on the various enamel surfaces, the surfaces showed (*a*) no attack, (*b*) a slight iridescence or loss of gloss, (*c*) a decided etch, or, in some cases, (*d*) the deposition of a hard, insoluble residue on the enamel coating. The action of the salt solutions is dependent on one or more of the following factors: (i) the nature of the ions released by the hydrolysis of the salts, (ii) the degree of dissociation of the respective ions, (iii) the effect of secondary dissociation, (iv) the effect of ions leached out or released from the enamel coating, and (v) the deposition of insoluble precipitates either in the solution or on the enamel surfaces.

## VI. Summary of Results

(1) Many previous investigators have used the loss-in-weight method, with a definite but single time period, in determining acid attack. The results of the present investigation show that a far more accurate picture of chemical action is obtained when the loss in weight is measured after several successive time periods and the chemical durability curve, loss in weight against time, is plotted.

(2) The loss-in-weight method is a satisfactory means of studying the chemical attack of the inorganic and organic acids, the alkalis, and, to a lesser extent, the salt solutions at room and at boiling temperatures.

(3) The ground-coat enamel is as resistant (or more so) to acid attack as the other non-acid-resisting enamels.

(4) The antimony white cover enamel is considerably more resistant to acid attack than either the fluoride white cover or the zirconium white enamels.

(5) In general at room temperature, the non-acid-resisting enamels are attacked only slightly by concentrated sulfuric or phosphoric acids; they are attacked to a greater degree by concentrated nitric acid; and they are appreciably attacked by concentrated hydrochloric acid.

(6) The less concentrated mineral acid solutions, the 20%, 10%, and 1% strengths, show appreciable-to-rapid attack at room temperature on practically all of the non-acid-resisting enamel surfaces.

(7) Several of the organic acids show an appreci-

able amount of attack at room temperature on the non-acid-resisting enamels.

(8) Porcelain enamel surfaces are quite resistant to chemical attack by alkalis and salt solutions at room temperature.

(9) At room temperatures, acid-resistant white cover enamels are very resistant to the attack of inorganic and organic acids.

(10) Acid-resistant white cover enamels are attacked to a moderate extent by the boiling mineral acids (sulfuric, hydrochloric, nitric, and phosphoric), to a slightly less extent by boiling oxalic acid, to an even less degree by boiling solutions of citric, tartaric, malic, and lactic acids, while the boiling solutions of acetic, pyrogallic, and carbolic acids show almost no attack.

(11) The acidproof or chemical enamel is approximately three times as resistant to acid attack at boiling temperatures as the acid-resistant white cover enamels.

(12) Ground-coat enamels and all cover enamels, including acid-resistant and acidproof, show equally low resistance to the attack of a boiling sodium hydroxide solution.

(13) The action of the boiling salt solutions on the various enamel surfaces is quite specific. In general, salts, which on hydrolysis give a decided alkaline reaction, show appreciable attack on all of the enamel surfaces; and salts, which on hydrolysis give a distinct acid reaction, show practically no attack on the acid-resisting surfaces but a variable degree of attack on the non-acid-resisting enamels.

(14) In interpreting the mechanism of chemical attack on porcelain enamels, it is indicated that, since silica is the predominant constituent in these coatings, the silica would form a relatively loose random structural arrangement in which the constituents, such as B, Al, Na, K, Ca, and others, would either replace silicon or be distributed in the interstices of the structural network. When the porcelain enamel coating is subjected to chemical attack, either (*a*) the more soluble material would be selectively leached out of the network leaving a silica-enriched layer or (*b*) the silica structure would be attacked and decomposed. In the former, (*a*), the silica-enriched layer would be present as a gel-like material which, on drying, would shrink and pull apart, leaving the characteristic pattern of attack.

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# ALUNITE AS SOURCE OF SCUMMING ON STONEWARE BODY*

By Jan O. Knizek and H. Fetter

Abstract

A heavy, disagreeable scumming developed on a surface of stoneware articles. This scum, having the appearance of a wrinkled skin, prevented the body from taking the salt glaze on account of its refractory character. It consisted almost entirely of the mineral anorthite, and its formation is attributed to the alunite content of the clay.

## I. Introduction

### (1) Occurrence and Clay Characteristics

After one year of successful use of a white-firing clay, an unusual scum began to appear on the surface of stoneware articles manufactured from it. This scum, forming a heavy skinlike coating prevented the body from taking the salt glaze. The general appearance of various articles covered by the scum coating is shown in Fig. 1, and an enlarged surface of a faucet is presented in Fig. 2. As may be seen from these pictures, the scum coating apparently contracted less than the body and, consequently, it is wrinkled, resembling closely an old man's skin. The coating could be separated easily from the body by scratching it with a knife blade, leaving behind the well-vitrified body, which had properties almost identical to those of the body on which the scumming did not appear.

Because of the rare characteristics of the clay, some of its properties and its composition are presented.

(*A*) *Chemical and Mineralogical Composition:* The clay contains 35.8% of alumina and 6.13% of alkalis, chiefly represented by potassium. The percentage chemical analysis of the clay is as follows: $SiO_2$ 47.14, $Al_2O_3$ 35.83, $Fe_2O_3$ 1.81, CaO 0.92, MgO 0.51, $K_2O$ 5.06, $Na_2O$ 1.07, $SO_3$ 1.34, and loss on ignition 6.44, a total of 100.12%. According to the thermal analysis† (see Fig. 3), the material seems to be composed of about 20 to 30% of the mineral kaolinite, the remainder being some thermally inert material. This finding has been confirmed later by the results of microscopical examination, which revealed the presence of about 60% of residual glass, 25% of clay particles, and 10 to 15% of alunite crystals. The latter appeared generally to fill pores and a minute fraction, the predominating size of alunite crystals, ranging from 30 to 90 microns. The indices of refraction ($n$) of the various materials contained in the clay were (1) residual glass 1.54 to 1.57 (natural glasses of the type to be expected here are considerably below this range) and (2) crystals, 1.57 to 1.60 (alunite, $\omega$ 1.572 and $\epsilon$ 1.592).

(*B*) *Plastic and Drying Properties:* For a material containing about 70 to 75% of nonplastic substances (residual glass and alunite), the plasticity was sur-

* Supplementary title No. 9 to Forty-Seventh Annual Program, The American Ceramic Society, 1945, *Bull. Amer. Ceram. Soc.*, **24** [5] 180 (1945). Received April 26, 1945.

† Thermal analyses were made at the Massachusetts Institute of Technology through the courtesy of F. H. Norton.

prisingly good. The transverse strength, as determined on bars 9 by 2 by 1 in. in size made in plaster of Paris molds from a body aged ten days and containing 24.8% of water (water of plasticity), was 284 lb. per sq. in., which again may be considered to be high; the drying shrinkage of 8.7% was also rather high.

(*C*) *Particle-Size Distribution:* The good plastic properties and relatively high transverse strength and drying shrinkage are certainly related to the extreme fineness of the material. The particle-size distribution determined by the ordinary pipette method described by Bray[1] is shown in Table I and Figs. 4 and 5. The alunite content of the clay was almost completely removed by screening the slurry through a 200-mesh sieve prior to the determination of the particle-size distribution. A microscopic examination of the residue left on a 200-mesh sieve showed it to be composed almost exclusively of alunite, the predominating crystal size being 90 microns with an index of refraction of between 1.56 and 1.58.

(*D*) *Firing Properties:* It is evident from Fig. 6 that the vitrification progresses rather fast, the vitrifying point being reached at cone 1. The highest values for fired transverse strength and firing shrinkage, 3034 lb. per sq. in. and 22.5%, respectively, were reached at

[1] R. H. Bray, "Significance of Particle Size Within the Clay Fraction," *Jour. Amer. Ceram. Soc.*, **20** [8] 257–61 (1937).

FIG. 1.—General appearance of the article covered by scum.

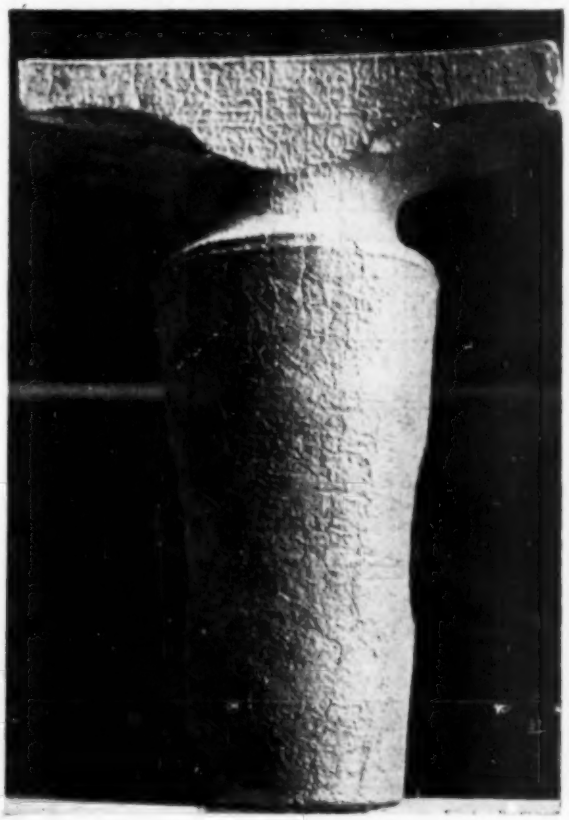

FIG. 2.—Enlarged surface showing wrinkled skinlike scum.

TABLE I

PARTICLE-SIZE DISTRIBUTION, TIME, AND DEPTH OF SAMPLING*

| Sampling depth (cm.) | Time | | Equivalent diam. (μ) | Finer than size (%) |
|---|---|---|---|---|
| | Hr. | Min. | | |
| 24.2 | 0 | 1 | 30 | 10.5 |
| 21.5 | 0 | 2 | 20 | 7.6 |
| 18.2 | 0 | 3 | 15 | 8.4 |
| 21.5 | 0 | 8 | 10 | 14.6 |
| 20.2 | 0 | 30 | 5 | 7.9 |
| 21.8 | 1 | 30 | 3 | 1.1 |
| 19.4 | 3 | 0 | 2 | 7.3 |
| 12.9 | 8 | 0 | 1 | 6.5 |
| 19.4 | 48 | 0 | 0.5 | 24.3 |

* Temp., 23°C.

FIG. 3.—Thermal-analysis curve of the clay.

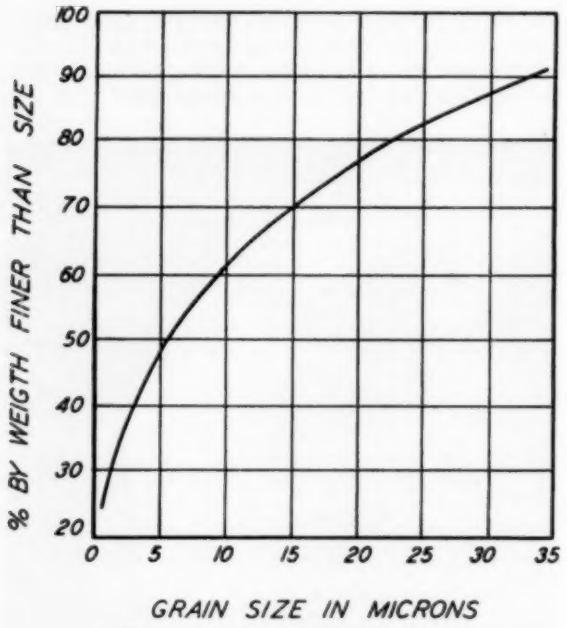


FIG. 4.—Particle-size distribution.

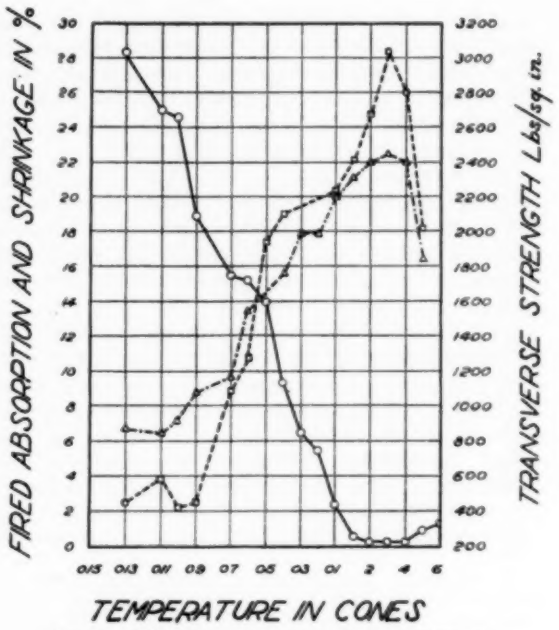


FIG. 6.—Firing properties vs. heat-treatment.

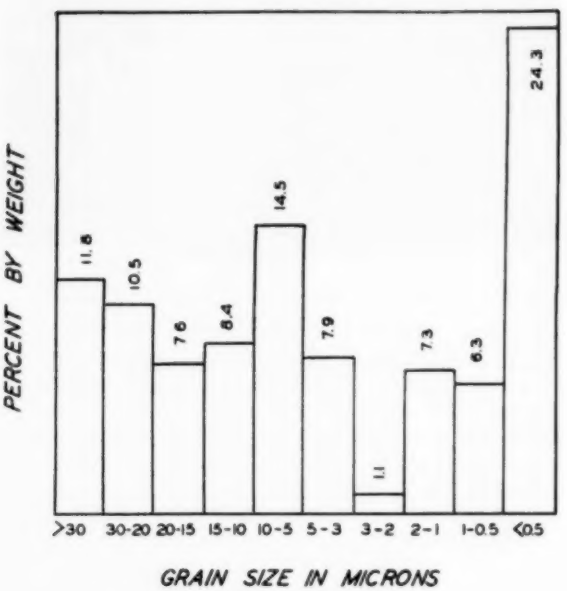


FIG. 5.—Particle-size distribution.

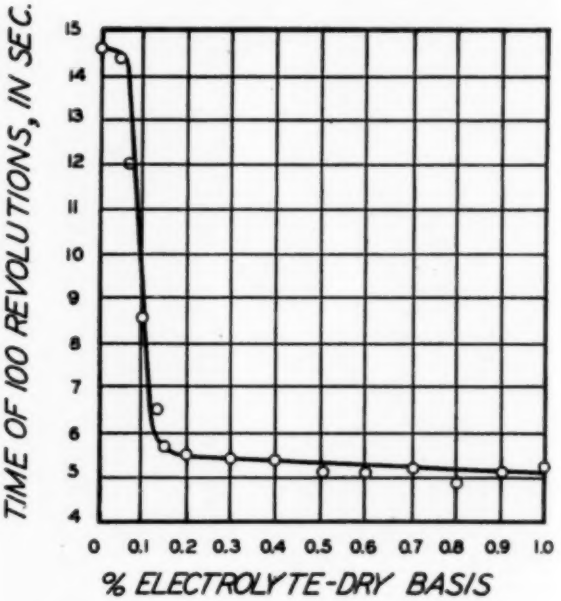


FIG. 7.—Slip fluidity vs. electrolyte concentration.

cone 3. The rapid progress of vitrification is explained by the presence of a large amount of finely divided alkali-rich glass. The alkalis contained in this material act with much more energy than those contained in or added to a clay body in the form of feldspar because of their more advantageous position, being present in combination with the silica and alumina in the glass even without application of heat. Approximately at cone 5, a spongy structure begins to develop, as may be seen from the increase of absorption. This bloating is undoubtedly caused by the volatilization of the alkalis. After firing a lump of the raw clay to cone 2, its appearance closely resembles opal glass, being white with a lustrous fracture and very translucent. Petrographic examination of a thin section showed that the alunite had disappeared completely. The material was transparent and chiefly homogeneous. Glass fields are cut by numerous small masses of pseudomorphs of original clay particles. The amount of glass after firing was estimated to 80%.

(*F*) *Exchangeable Bases and Casting Properties:* The exchangeable bases were determined by using the

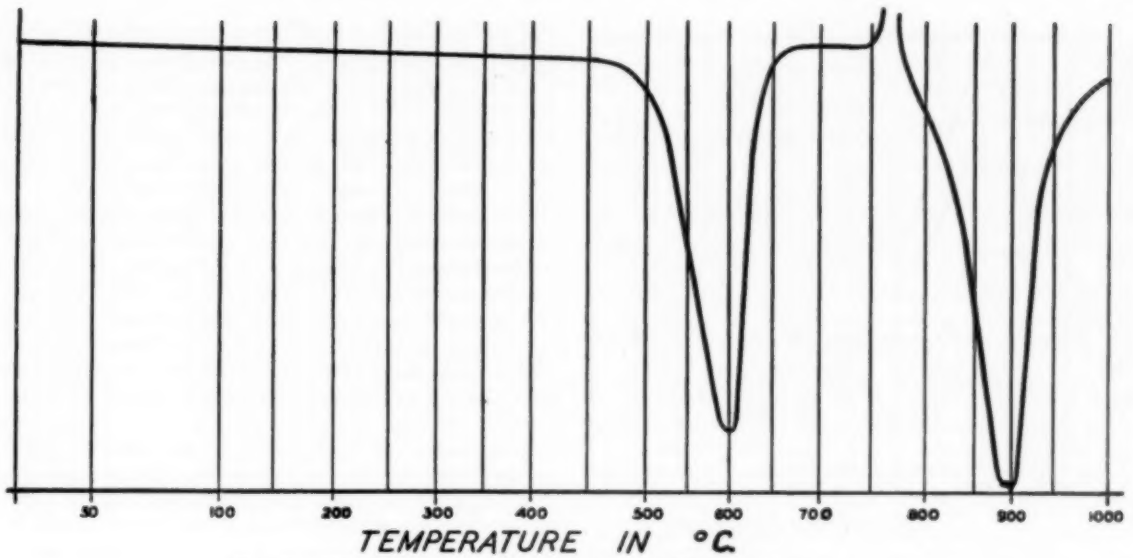


FIG. 8.—Thermal-analysis curve of a typical Mexican alunite.

method of Graham and Sullivan.[2] An analysis of exchanged bases in milliequivalents per 100 gm. of clay was as follows: Calcium 3.9, magnesium 0.0, sodium 0.2, potassium 3.6, a total of 7.7 exchanged cations, and $SO_4$ 1.2. The value of this result is rather doubtful because of the presence of relatively large amounts of soluble salts.

The behavior toward the addition of electrolytes is another desirable property of the material. Complete deflocculation of a slip containing 40% of solids and 1% of $BaCO_3$ was accomplished by an addition of 0.15 to 0.20% of a commercial 40°Bé Na silicate. This is evident from Fig. 7, where the recorded time in seconds of 100 revolutions of the Stormer viscometer driven by a weight of 250 gm. was plotted against the Na silicate concentration. The sudden drop of viscosity from 14.5 seconds per 100 revolutions to 5.7 seconds per 100 revolutions at a concentration of 0.15% Na silicate is quite remarkable, supposing only 30% of the material is affected by electrolyte additions. The addition of $BaCO_3$ to the slip was necessary to eliminate from the system the $SO_4''$ ion which otherwise inhibits the ion exchange.

### (2) Body Characteristics, Firing, and Glazing

Owing to the quite high drying and firing shrinkage of the used clay, the grog content of the body was 40%. It was prepared by calcining the clay in lump form through a tunnel kiln to cone 2 approximately. After this treatment, the clay was well vitrified and white, closely resembling white opal glass. The grog and the raw clay were ground to 36-mesh size. The mud was prepared in an 8-ft. wet pan, and the usual chemical stoneware products were made either by hand turning on a potter's wheel or by hand molding into plaster of Paris molds.

[2] R. P. Graham and J. D. Sullivan, "Critical Study of Methods of Determining Exchangeable Bases in Clays," *Jour. Amer. Ceram. Soc.*, **21** [5] 176–83 (1938).

TABLE II
COMPARISON OF CHEMICAL ANALYSIS OF SCUM AND THEORETICAL COMPOSITION OF ANORTHITE

| | Scum (%) | Anorthite (%) |
|---|---|---|
| $SiO_2$ | 40.50 | 43.2 |
| $Al_2O_3 + Fe_2O_3$ | 33.70 | 36.6 |
| CaO | 20.60 | 20.2 |
| MgO | 1.02 | |
| $SO_3$ | 1.86 | |
| $K_2O$ | 2.10 | |
| | 99.78 | 100.0 |

The ware was fired in an oil-fired, round downdraft 32-ft. kiln to cone 2, following a firing schedule of 96 hours. Although the kiln is usually fired under reducing conditions, it was found that the scum appeared indistinctly under reducing or oxidizing conditions.

The ware was salt glazed, using both common salt and borax. The salting procedure consisted of two rounds each hour, throwing one shovel into the furnace of each kiln. Four rounds of common salt were followed with one of borax. Usually eight rounds had to be made before a satisfactory glaze was obtained.

### (3) Body Properties

The properties of the body were as follows: porosity, 0.5%; modulus of rupture, 4500 lb. per sq. in.; and compressive strength, 51.475 lb. per sq. in. Owing to the reducing condition which prevailed throughout the entire firing period, the body color was light gray. The body, in spite of its unsatisfactory $Al_2O_3$ to $SO_3$ molecular ratio of 1 to 2.232,[3] took a thin but uniform and quite bright salt glaze.

## II. Source of Scum

### (1) Examination of Scum

To investigate the nature of this unusual form of scumming, the dust removed by scratching the body

[3] L. E. Barringer, "Relations Between Constitution of Clay and Its Ability to Take a Good Salt Glaze," *Trans. Amer. Ceram. Soc.*, **4**, 211–29 (1902).

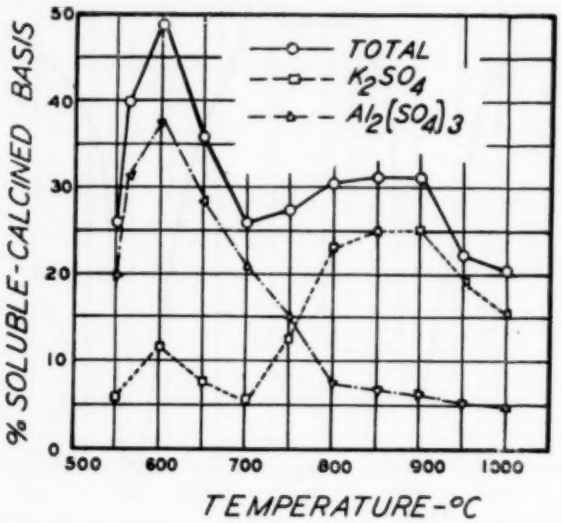


FIG. 9.—Solubility of a typical alunite vs. heat-treatment.

surface was analyzed and examined by means of a petrographic microscope. Because of the possibility that the original characteristics of the scum taken from a body which was subjected to salt glaze might have been changed to some degree, the scum was removed from a body that was fired to the same degree without subsequent salt glazing. In Table II, the chemical analysis of the scum is compared with the theoretical composition of anorthite.

In determining the optical properties, it was found that about 90 to 95% had an index of refraction of 1.56 to 1.63 (anorthite $n$ is 1.56). Only about 50% clearly showed an extinction with crossed Nicols and, therefore, indicated crystalline structure, but this may be due to the orientation of the crystals; the material, moreover, is soluble in HCl.

Table II shows that the chemical composition of the scum closely approaches that of anorthite and the index of refraction is the same as that of anorthite, so there seems to be little doubt that the scum formed on the surface of the fired clay is anorthite.

### (2) Clay Examination

A representative sample of the new clay shipment was examined by means of a petrographic microscope to detect any change in the mineralogical composition of the material. It was found that, in comparison with the first shipment, the alunite content increased from 15% to about 25%. The alunite was found chiefly in grains of about 60 microns; the remainder was again residual glass and clay.

## III. Mechanism of Scum Formation

The results obtained seem to indicate that the alunite is to be blamed for the scum formation. According to Fink, Van Horn, and Pazour[4] and Ogburn and Stere,[5] the decomposition of alunite is accomplished in two stages. At about 460°C., the loss of water of combination is completed and the alunite is transformed into dehydrated alum which slowly recrystallizes, the recrystallization being completed at about 700°C. From 700° to 800°C., the dehydrated alum decomposes into alpha-$Al_2O_3$ and potassium sulfate, which remains without change, and at higher temperatures partly volatilizes and partly combines with the alumina to form potassium aluminate. The actual temperature of decomposition of alunite minerals probably varies among the samples. For example, when a typical Mexican alunite has been subjected to thermal analysis, the thermal curve shown in Fig. 8 was obtained. The first very pronounced endothermic effect at about 600°C. corresponds to the formation of dehydrated alum; the second effect, still more pronounced, possibly corresponds to the decomposition of alum and the formation of alumina and potassium sulfate. This assumption seems to be further supported by the results of the solubility test* verified on samples fired at different temperatures. The corresponding curve in Fig. 9 shows a definite peak in solubility of the aluminum sulfate at 600°C. and a sudden increase in that of the potassium sulfate between 700° and 900°C., where the maximum is reached. The only important fact is that above 900°C. the $K_2SO_4$ is still present. Fink, Van Horn, and Pazour[4] found a sharp reflection of $K_2SO_4$ at 1000°C. The melting point of $K_2SO_4$ is given as 1067°C.[6] The possible explanation of the scum formation is that the fused potassium sulfate begins to migrate to the surface as soon as the porosity decreases and the body approaches its vitrification point. The molten potassium sulfate dissolves the calcium sulfate that is present. The silica and alumina are provided either in the same way or just by reaction with the clay surface. There the potassium sulfate volatilizes, leaving a residue composed essentially of calcium oxide, alumina, and silica.

According to Clarke,[7] of all feldspars, anorthite is most easily made artificially.

> In the investigation by Day and Allen . . . it was prepared without difficulty by simply fusing its constituent oxides together; and this observation is in accord with the results obtained by previous experimenters. Vogt observed its formation in slags, and Morozewicz repeatedly obtained feldspars varying from labradorite to nearly pure anorthite in his experiments with artificial magmas. Fouqué and Lévy obtained anorthite directly from its constituents; and Meunier, upon fusing silica, lime, and aluminum fluoride together, found sillimanite, tridymite, and anorthite in the resultant mass. Anorthite is also formed by the breaking down of other more complex silicates. Des Cloizeaux, by fusing garnet and vesuvianite, obtained crystals which Fouqué and Lévy identified as anorthite; and similar results are reported, with much

[4] W. L. Fink, K. R. Van Horn, and H. A. Pazour, "Thermal Decomposition of Alunite," *Ind. Eng. Chem.*, **23** [11] 1248–50 (1931); *Ceram. Abs.*, **11** [4] 274 (1932).

[5] S. C. Ogburn, Jr., and H. B. Stere, "Thermal Decomposition of Alunite," *Ind. Eng. Chem.*, **24** [3] 288–89 (1932) *Ceram. Abs.*, **11** [10] 530 (1932).

* Data on solubility and thermal behavior of alunite were taken from an unpublished study.

[6] International Critical Tables, Vol. I. p. 154.

[7] F. W. Clarke, "Data of Geochemistry," *U. S. Geol. Survey Bull.*, No. 770, 5th ed., 841 pp. (1924); p. 368. In the present citation from Clarke's book, the initials and reference numbers of the men whose works are cited have been deleted.

more detail, by Doelter and Hussak. Doelter also found anorthite among the products formed by fusing epidote, axinite, chabazite, and scolecite. Finally, Friedel prepared anorthite in the wet way by heating muscovite with lime, calcium chloride, and a little water to 500° in a steel tube.

Taking into consideration the ease with which anorthite is formed from its constituents, it seems to be quite understandable in the present case how this compound may have been formed at relatively low temperatures. The molten potassium sulfate may have taken first into solution the present calcium sulfate (artificial syngenite $CaK_2(SO_4)_2H_2O$ is easily made by direct action of potassium sulfate upon gypsum*). Afterward, the molten mixture of potassium and calcium sulfate possibly dissolved a part of the alumina and silica before migrating to the surface. Silica, alumina, and calcium oxide then met in the molten potassium sulfate, and anorthite was formed after or perhaps before the volatilization of the former.

* See Clarke, p. 228 of footnote 7.

## IV. Summary

The scum coating which appeared on a stoneware body on firing proved to be composed essentially of the mineral anorthite as determined by chemical analysis and microscopic examination.

The substance to be blamed for the scum formation seems to be the alunite, which has been found in the clay in exceedingly large quantities. Although the alunite content of the clay remained at 15%, no troubles have been observed from its presence. The explanation for the scum-formation mechanism is that the potassium sulfate, which remains as the only soluble and readily fusible compound after the decomposition of the alunite, dissolves the calcium sulfate, alumina, and silica and migrates to the surface at temperatures closely approaching that of the clay vitrifying point. The anorthite may easily crystallize out of the melt of the potassium sulfate, which is volatilized and disappears completely.

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# USE OF WOOD ASH IN A LOW-FIRE MAT GLAZE*

By Haldon L. Thurn

Abstract

The development of a low-fire mat glaze for studio use is described in which part of the fluxes and silica and alumina are supplied by the use of wood ash. The materials required are simple and readily obtained and the glaze is easy to apply. One firing is eliminated by its application to the green ware, and the firing range is from cones 04 to 02.

## I. Introduction

A low-fire mat glaze has been developed in which wood ash is one of the principal ingredients. The glaze matures at cones 04 to 02 and yet retains, insofar as possible, the qualities of a stoneware-ash glaze, which was the source of its inspiration. The desired qualities were simplicity of preparation, ease of application, and the necessity of only a single firing.

## II. Historic Background

For centuries, the Oriental potters, notably the Chinese and later the Japanese, have used wood ash as a fluxing material in their stoneware and porcelain glazes. "How and when they discovered the use of this material is unknown, but since wood was the material used for firing the kilns, the resulting glost areas in the kiln probably suggested the idea."[1]

In the western world, the use of wood ash as a fluxing material in glazes was probably introduced in England by Bernard Leach on his return from the Orient. In the United States, Maija Grotell has done much to encourage its use.

Comparatively little has been written about the use of wood ash. The orientals have written nothing that has been translated for practical use; the Encyclopedia Britannica[1] mentions it in an article on Chinese glazes; and Heatherington[2] speaks of its use in his book on Chinese ceramic glazes. Leach[3] is the only person to have written informatively of its use in stoneware glazes. The author knows of no publication in which its use in low-fire glazes has been described.

## III. Preparation of Bodies and Glazes

Wood ash supplies the glaze with a certain amount of silica, alumina, and fluxes, principally potassium, calcium, and magnesium, as well as small amounts of iron, copper, and phosphorous. The proportion of alumina and silica to the alkalis in the ash determines to a large extent the quality of the glaze. Ashes from almost any wood or vegetable source may be used. In most cases, ashes from different plants and trees will have varying amounts of the alumina, silica, and alkaline combination, resulting in a slightly different but always interesting texture in the glaze. Mixed wood ash is excellent, and the variation from one gathering to the next will be so slight that little or no difference will be found in the glaze.

The fireplace is a good place to secure ash, or wood may be burned in the open. In gathering the ash, care should be taken to avoid foreign matter, and paper should be used sparingly to start the fire as any quantity

* Forty-Seventh Annual Program, The American Ceramic Society, 1945 (Design Division, No. 2); presented at the Chicago Local Section Meeting, April 7, 1945. Received April 6, 1945.

[1] Encyclopedia Britannica, 14th ed., Vol. 18, p. 361.

[2] A. L. Heatherington, Chinese Ceramic Glazes. Cambridge Univ. Press, England, 1937.

[3] Bernard Leach, A Potters Book, pp. 159–64. Faber & Faber, Ltd., 24 Russell Sq., London, 1940.

of paper ash will cause the glaze to have the appearance of a slip englobe. The amount of china clay used in papermaking upsets the balance in the glaze.

The ashes are prepared by sieving and washing to remove solubles and such foreign matter as charcoal and sand. The sieved ashes should be washed until the water, after the ash has settled, is clear and tasteless. This will occur after 15 to 20 waters. Care should be taken in sieving ashes as the potash content can cause serious burns to the hands.

The following procedure for sieving the ashes is suggested: Place a 20-mesh sieve over a large container; fill the sieve with ashes and play a gentle stream of water over them to wash the ash through the sieve; allow the ashes to settle, and repeat the process through a 40-mesh sieve and then through a 60-mesh sieve. The three sieves will remove all foreign matter of an injurious nature.

Sieves up to 100-mesh were used in this experiment, but no advantage was found in using the finer sieves; 60-mesh sieves were therefore adopted as standard for this glaze.

One of the requirements is that the procedure of the glaze preparation be kept simple. In addition to the ash, the glaze ingredients were white lead, Tennessee feldspar, flint, English ball clay, and calcined china clay. The flint and whiting content, however, were gradually reduced until they were entirely eliminated.

Four clay bodies prepared for use in the trials were as follows:

| | Body | | | |
|---|---|---|---|---|
| | No. 1 (lb.) | No. 2 (lb.) | No. 3 (lb.) | No. 4 (lb.) |
| Amaco clay* | 10 | 10 | | |
| Fine grog | 2.5 | | 2.5 | |
| Lake Michigan sand | | 2.5 | | 2.5 |
| Jordan clay† | | | 10 | 10 |

* American Art Clay Co., Indianapolis, Ind.
† United Clay Mines Corp., Trenton, N. J.

All four bodies were satisfactory, but those containing the Lake Michigan sand seemed to be somewhat harder. All of the clays worked well on the potters' wheel; and all tests were made on samples pressed in a plaster mold. The finished pieces were made on the potters' wheel, and the glaze was tested on the bisque-fired pieces as well as on the green ware. The firing results were similar on all bodies.

### (1) Glaze Application and Firing

Glaze application was easier on the green ware and no cracks appeared in the drying; it was more difficult to get an even coat on the bisque ware except by spraying. The glaze may be applied by brushing, pouring, or spraying; brushing, however, is preferable on green ware because the ware is glazed in the leather-hard stage.

Pouring or spraying must be done very carefully because the ware is saturated with moisture and is easily deformed. If the glaze is applied with a brush, three to five coats are required when the glaze has the consistency of thick cream; application should be made to about the same thickness as would be used for a bright glaze but never as thick as for the standard mat glazes.

No crawling has ever occurred on any pieces glazed by this formula.

All firing was done in the usual manner, and tests were made in two kilns, one of medium size and a large kiln. Maturity was reached at cone 04 in the smaller kiln where the heat rise was comparatively rapid. In the larger kiln, where the firing period was longer and the heat rise slow, a cone 02 temperature was required.

## IV. Specific Tests

Five series of tests were necessary to develop the glaze. The first and third series were compounded separately; the second, fourth, and fifth series were triaxials of twenty-one samples each. The materials were weighed in grams on a good balance and ground by hand in a wedgwood mortar; one-half hour of grinding was necessary for the large batches and fifteen minutes for the small samples.

### (1) Series A Glazes

Seventeen glazes were compounded for series A; none of this series was satisfactory. The tests showed, however, that there was nothing inherent in the wood ash that would prevent it from being used in low-fire glazes. Glaze A–8 played its part in the eventual solution of the problem. Four glazes of series A are listed.

| | Batch weights for series A glazes | | | |
|---|---|---|---|---|
| | A–8 | A–12 | A–14 | A–17 |
| White lead | 33.3 | 50.0 | 36.4 | 32.6 |
| Wood ash | 16.6 | 16.7 | 36.4 | 34.9 |
| Feldspar | 33.3 | 16.7 | 18.2 | 16.3 |
| Ball clay | 16.6 | 8.3 | | 11.6 |
| Flint | | 8.3 | 9.1 | 4.6 |
| | 99.8 | 100.0 | 100.1 | 100.0 |

Glaze A–8 was mat but immature; A–12 matured but was glossy; A–14 was glossy but immature; and A–17 was mat but immature. At this time, A–17 was considered to be the best of the series.

### (2) Series B Glazes

A triaxial was used for the B series. For the end members, a glaze maturing at cone 09, the stoneware ash glaze, and glaze A–17 were used. From these three widely divergent glazes it was hoped a happy medium would be found. These batches were weighed out, ground, and prepared as in series A, and the samples were fired to cone 04.

| | Batch weights for end members series B | | |
|---|---|---|---|
| | B–1 | B–16 | B–21 |
| White lead | 60.0 | | 32.6 |
| Wood ash | | 40.0 | 34.9 |
| Feldspar | 25.0 | 40.0 | 16.3 |
| Ball clay | | 20.0 | 11.6 |
| Flint | 12.0 | | 4.6 |
| Whiting | 2.4 | | |
| | 99.4 | 100.0 | 100.0 |

Glaze B–2 was glossy with a slight tendency toward mat, and innumerable pinholes were found wherever the glaze was a bit thick; B–3 was glossy and slightly crazed; B–4, a sugary mat with small pinholes; B–6 and B–7, rough mats; B–9, a good stony mat; and B–10 only a little less good. The remainder of the samples was underfired.

Samples of glazes B–9 and B–10 were made and placed in various parts of the kiln. Those near the flues of the kiln had a bright cheek on the side next to the tubes; but those in the center came out good, which indicated that the glaze either had a very narrow firing range or that the flint content was too high.

| | Batch weights | |
|---|---|---|
| | B–9 | B–10 |
| White lead | 39.3 | 43.6 |
| Wood ash | 21.5 | 21.8 |
| Feldspar | 23.4 | 19.8 |
| Whiting | 0.9 | 0.9 |
| Ball clay | 8.4 | 7.3 |
| Flint | 6.4 | 6.6 |
| | 99.9 | 100.0 |

## (3) Study of Ashes

Having failed to secure a stable glaze in the two series of tests, the analyses of a number of ashes as given by Leach[3] were studied. It was found that of the fluxes contained in wood ash calcium was by far the most important, magnesia second, and potash last. Six samples based on successful mat glazes were prepared, allowing the calcium content of each glaze to determine the amount of wood ash used. A composite formula of the ashes listed was made to assist in arriving at these amounts. Since the composite ash formula could only be an approximation of the ash being used and probably would not result in a perfect glaze, it was hoped that something would be secured that would point the way to eventual success.

## (4) Series C Glazes

Six glazes were prepared and fired. Two of these trials, which contained a small amount of zinc and had a disagreeable color, were discarded; another crawled; a fourth, which was comparatively high in flint, was full of pinholes. The first and last of the six glazes had good color; the first (C–1) was semimat and the last (C–6) a sugary mat.

## (5) Series D Glazes

Believing that with slight adjustments in glazes C–1 and C–6 the glaze being sought would be found, a second triaxial (series D) was planned, using B–5 as the third member of the group. This glaze was chosen, in spite of its high flint content, because of its texture.

| | Batch weights for end members, series D | | |
|---|---|---|---|
| | C–1 | C–6 | B–5 |
| White lead | 54.9 | 47.3 | 48.2 |
| Wood ash | 10.1 | 12.7 | 14.5 |
| Whiting | | | 1.4 |
| Feldspar | 18.0 | 28.0 | 22.2 |
| Ball clay | 6.8 | 12.0 | 4.8 |
| Calcined clay | 7.2 | | |
| Flint | 3.0 | | 8.7 |
| | 100.0 | 100.0 | 99.8 |

None of these fired samples lacked interest, none was immature, and there were no pinholes or bubbles. Glazes D–2, D–3, and D–4 were good semimats; D–7, a good mat; D–11, mat but a runny glaze; D–12, D–15, and D–16, partly mat; the remainder of the glazes was glossy.

The mat samples were completely lacking in whiting and the flint content was negligible. It was concluded therefore that the silica content of the glaze must be supplied entirely by the ash, clay, and feldspar.

## (6) Series E Glazes

Keeping glazes C–1 and C–6 in their respective places and replacing B–5 with A–8, series E was prepared; glaze A–8 was selected because it was a viscous glaze, completely lacking both whiting and flint; its big advantage was its low content of white lead and high feldspar content. Glaze C–1 had reverse composition. With these favorable mixes plus the influence of C–6, it was hoped that a good glaze would be produced. The C–1 and C–6 combinations were not repeated. The fired C–6 and A–8 combinations were underfired. Of the remaining tests, E–3 was dull and uninteresting; E–5 was semimat; and E–9, E–10, E–12, and E–13 were excellent mats. They possessed the stonelike quality and the waxlike sheen of the stoneware glaze. The recipe was simple; the flint content had been reduced to a negligible amount.

Samples were made of the four glazes (E–9, E–10, E–12, and E–13) omitting flint; the appearance was not impaired by its omission, and flint was dropped from the recipe. Batch weights for these four glazes without flint are as follows.

| | Batch weights for series E (without flint) | | | |
|---|---|---|---|---|
| | E–9 | E–10 | E–12 | E–13 |
| White lead | 43.9 | 41.6 | 45.7 | 42.8 |
| Wood ash | 13.4 | 14.5 | 13.2 | 14.0 |
| Feldspar | 27.8 | 28.1 | 27.6 | 28.6 |
| Ball clay | 12.1 | 13.2 | 12.1 | 13.2 |
| Calcined clay | 2.8 | 2.6 | 1.4 | 1.4 |
| | 100.0 | 100.0 | 100.0 | 100.0 |

Glaze E–12 possessed the best qualities of the four. All further experimenting was done with this glaze.

Ashes from a fireplace at Cranbrook were used throughout these experiments. Ashes also have been obtained and tested from a fireplace in New Jersey and from one in Milwaukee as well as those from a brush heap and from various leaves, grasses, and plants, totaling fifteen, with no change in the recipe. Little or no difference could be found in the quality of glaze in any case.

# V. Color

The glaze is extremely sensitive to most coloring oxides. A list of a number of colors which have proved successful is given. Three tests were made for each color. In each case, the oxide was added to 100 gm. of

glaze and ground in a wedgwood mortar for one-half hour. For sample (*a*), full strength was used; sample (*b*), five parts colored to five parts uncolored; and for sample (*c*), two parts colored to eight parts uncolored. In most cases, (*c*), the third of the series was the best.

(1) Cobalt oxide 4 gm., zinc oxide 4 gm.: (*a*) very dark blue, almost black, (*b*) dark blue, and (*c*) medium blue.

(2) Cobalt oxide 1 gm., nickle oxide $1^1/_2$ gm.: (*a*) soft blue, deep in value, (*b*) lighter and more grayed, and (*c*) gray-blue.

(3) Copper oxide 4 gm., cobalt oxide 1 gm.: (*a*) very dark blue-green, (*b*) lighter and richer, and (*c*) grayed.

(4) Copper oxide 2 gm., manganese carbonate 5 gm.: (*a*) dark green, rough and uninteresting, (*b*) light cool green, and (*c*) very light green.

(5) Copper oxide 3 gm., red iron oxide 1 gm.: (*a*) dark dirty green, (*b*) rich dark green, and (*c*) lighter and grayer.

(6) Copper oxide 3 gm., red iron oxide $1^1/_2$ gm., and nickle oxide 1 gm.: (*a*) dirty brownish green, (*b*) rich warm dark green, and (*c*) yellow-green.

(7) Manganese carbonate 8 gm., copper oxide 1 gm.: (*a*) dark metallic brown, (*b*) mahogany brown, and (*c*) dark tan.

(8) Manganese carbonate 6 gm., red iron oxide 2 gm.: (*a*) very dark brown, (*b*) warm dark brown, (*c*) pinkish tan.

(9) Nickle oxide $2^1/_2$ gm., manganese carbonate $1^1/_2$ gm.: (*a*) dark brown, (*b*) brown, and (*c*) tan.

(10) Pink stain 10 gm.: (*a*) dark purplish red, (*b*) lighter, and (*c*) grayed pink.

(11) Uranium oxide 10 gm.: (*a*) dark orange-brown, (*b*) orange, and (*c*) yellow-orange.

(12) Naples yellow 10 gm: (*a*) yellow, (*b*) pale yellow, and (*c*) ivory-yellow.

## VI. Summary

In the glaze described, wood ash supplies a part of the silica and alumina content along with certain fluxes of which calcium is the more important.

In the alumina-type mats, wood ash produces a texture similar to that of the stoneware glaze which was the source of inspiration.

The glaze can be applied by brushing, pouring, or spraying on the green ware or on bisque-fire ware; brushing on the unfired ware is preferable. An overthick application destroys the beauty of the glaze.

The glaze does not crawl and it is self-healing when drying cracks appear; no cracks, however, have appeared when the glaze has been used on green ware. Handsome colors can be produced with the use of very little coloring oxide.

### Acknowledgment

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## TRUSTEES FROM INDUSTRIAL DIVISIONS*

*Design:* W. A. Weldon, Locke Insulator Corp., Baltimore 3, Md (1946)
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*Materials and Equipment:* E. M. Rupp, 410 Northridge Rd., Columbus 2, Ohio (1948)
*Refractories:* J. B. Austin, U. S. Steel Corp., Kearny, N. J. (1946)
*Structural Clay Products:* J. H. Isenhour, Isenhour Brick & Tile Co., Salisbury, N. C. (1948)
*White Wares:* J. W. Hepplewhite, Edwin M. Knowles China Co., Newell, W. Va. (1947)
*Institute of Ceramic Engineers:* H. M. Kraner, Bethlehem Steel Co., Bethlehem, Pa. (1947)
*Ceramic Educational Council:* R. M. Campbell, New York State College of Ceramics, Alfred, N. Y. (1947)

* Date of expiration of term of office in parentheses.

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*Chairman:* W. W. Higgins, A. O. Smith Corp., Milwaukee 1, Wis.
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**Glass**
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*Secretary:* S. R. Scholes, N. Y. State College of Ceramics, Alfred, N. Y.

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**Refractories**
*Chairman:* S. M. Swain, North American Refractories Co., Cleveland 14, Ohio
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## INSTITUTE OF CERAMIC ENGINEERS

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